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16. ABSTRACT The report gives results of an extensive review and analysis of the literature aimed at: studying historical trends of particulate, SOx, and NOx emissions and of acid rain in the northeastern U.S.; studying size and composition of particulates from power plants; and analyzing interactions between particulates and sulfur-bearing gases from coal-fired power plants. Particulate mass emissions from industrial and combustion sources project a rising trend, nationwide, if no additional controls are assumed. (With application of best controls, the trend projection is reversed.) SO2 emissions have been increasing nationwide since 1950; without additional controls and with a 5% industry growth, this trend is expected to continue. (If new source performance standards and state implementation plans become effective in 1978, SO2 emissions are expected to decrease.) NOx mass emissions have increased consistently since 1920; those for 1970 were more than 3 times those for 1920. The limited data available for ambient NOx levels is further complicated by inherent limitations of measurement techniques used to obtain the data. Information on acid rain in northeastern U.S. is extremely scarce. Available data indicates that precipitation in this region has become increasingly acidic over the years. A better assessment of the trend can be made only when better rainwater pH information becomes available.

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Rain	Electric Power Plants	Stationary Sources	04A
Acidity	Coal	Acid Rain	07D 10B
Dust	Combustion	Particulate	11G 21D
Sulfur Oxides			07B 21B
Nitrogen Oxides			

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PARTICLE EMISSION REACTIVITY

by

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The authors sincerely appreciate the helpful suggestions provided by Dr. L. J. Shannon and Mr. M. P. Schrag in completing this task.

SUMMARY

This task was undertaken by Midwest Research Institute for the Environmental Protection Agency. The purposes of this task were (a) to study historical trends of particulate, SO_x and NO_x emissions and of acid rain in the northeastern United States; (b) to study particle size and composition of particulates from power plants; and (c) to analyze interactions between particulates and sulfur-bearing gases from coal-fired power plants.

An extensive review and analysis of the literature was conducted to accomplish the above objectives. Pollutant emission trends were examined based on mass emissions as well as ambient levels in northeastern sections of the United States. Acid rain trends were studied based on available information reporting pH of rainwater for various cities in the Northeast. Interactions between particulates and sulfur-bearing gases from coal-fired power plants were analyzed using potential reaction mechanisms and order-of-magnitude calculations for reaction rates for each mechanism based on reported data.

Particulate mass emissions from industrial and combustion sources project a rising trend, on a nationwide basis, if no additional controls are assumed. With application of best controls, the trend projection is reversed. There is a high concentration of particulate emissions in the northeastern United States. Data for 1972 indicate that 52% of the total U.S. particulate emissions are emitted in the northeastern region between the State of Illinois and the Atlantic seaboard lying to the north of the Tennessee-Mississippi border. However, particulate concentrations, both in the nation and in the northeastern region, show a decreasing trend during the 4-year period from 1970 to 1973.

SO_2 emissions have been increasing nationwide since 1950. With no additional controls and a 5% industry growth, this trend is expected to continue; but if new source performance standards (NSPS) and state implementation plans (SIP) become effective in 1978, then SO_2 emissions are expected to decrease. Northeastern United States has a high concentration of SO_2 emissions and the highest ambient levels of sulfates. However, existing data indicate a downward trend for ambient levels of SO_2 and sulfates for selected northeastern urban areas and an increasing trend for sulfates in nonurban areas.

NO_x mass emissions have increased consistently since 1920. Emissions for 1970 are more than three times of that observed for 1920. Only limited data are available for ambient levels of NO_x and this is further complicated by inherent limitations of measurement techniques used to obtain these data.

Information on acid rain in northeastern United States is extremely scarce. The available data indicate that precipitation in this region has become increasingly acidic over the years. A better assessment of the trend can only be made when additional information on rainwater pH and pH measurement techniques becomes available.

Analysis of fly ash particle size distributions and composition shows a preferential concentration of certain trace elements such as Pd, Cd, Se, As, V, Ni, etc., in the finer particles which are emitted to the atmosphere. Many of the trace elements are active catalysts for the oxidation of SO_2 to acid.

Interactions between particulates and sulfur-bearing gases from coal-fired power plants were studied by considering four reaction mechanisms. These mechanisms are absorption-oxidation of SO_2 by particulate, direct catalytic oxidation of SO_2 by particulate, adsorption/chemical reaction of SO_2 by particulate, and photolytic oxidation of SO_2. Absorption-oxidation refers to SO_2 oxidation catalyzed by particulates in the presence of significant amounts of water. Direct catalytic oxidation assumes minimal quantities of water, typically one monolayer of adsorbed water. Both of these mechanisms are acid generation processes. Adsorption/chemical reaction of SO_2 by particulate is a removal process whereby the precursor for acid formation is removed by physical adsorption or chemisorption. The last mechanism (photolytic oxidation) refers to SO_2 conversion in the presence of sunlight.

On the basis of data presented in this report, catalytic oxidation of SO_2 by absorption-oxidation and direct oxidation are both plausible mechanisms by which rapid SO_2 oxidation could occur. These reactions could take place at or near ground level in the absence of sunlight and need to be considered in predicting SO_2 oxidation in stack plumes. Although the list of catalytically active elements is far from complete, vanadium pentoxide is found to have a much higher activity than others for which data are presently available. SO_2 removal by adsorption is ruled out by the analysis and photolytic oxidation of SO_2, particularly in the presence of hydrocarbons and other oxidants, warrants further investigation.

Whether the increased use of particulate control systems on power plants or shifts in fuel usage have altered (positively or negatively) the regional acid rain trends in the northeastern U.S. are unanswered questions at this time. The substitution of oil for coal as a power plant fuel and the accompanying probable increase in vanadium (a very active catalyst for SO_2 oxidation) emissions may also work to counter the expected decrease in acid rain resulting from decreased SO_2 emissions achieved by fuel switching. Further study will be needed to answer these questions.

Future studies of the acid rain phenomenon should include a systematic evaluation of the various parameters such as catalyst type, concentration, temperature, relative humidity, etc., which affect the kinetics of SO_2 oxidation in order to identify the main rate-controlling factors. Acid rain formation from nitrates and chlorides should be separately investigated even though currently available information supports the hypothesis that only about 25% of the acidity in rain is due to nitrates and less than 10% due to chlorides. Refinement of techniques to predict whether sulfates, nitrates, or chlorides are contributory to the acidity in a particular rain sample should also be undertaken. The incorporation of mathematical modeling to include transportation effects of pollutants to areas of geographic interest and characterization of ambient particulates for size distribution and comparison are also recommended. Finally, meteorological methods which monitor rainfall in different states and regions of the U.S. should include pH measurement of rainwater on a routine basis if it is not already being done. This would eliminate the data gap that presently exists for some sections of the U.S. and for most sections on a recent basis.

INTRODUCTION

Increased acidity in rain and snow in the northeastern United States, Sweden, and other parts of Europe, is of growing concern due to its potential for ecological damage, adverse health effects and corrosion of materials. It is presently believed that anthropogenic factors are the major cause for the increased acidity. But one recent report claims that biogenic sources can contribute up to 50% to the annual mean sulfate levels near extensive bodies of (polluted) water.

Acid rain has been primarily attributed to industrial sulfurous emissions which result in increased sulfates in the atmosphere. Another important industrial emission is particulates which can act as nuclei and/or catalysts for the adsorption and reaction of sulfur dioxide to form sulfates. Ammonia, nitrates, and chlorides from industrial emissions can also contribute to acidity in rain but to a lesser extent.

The Environmental Protection Agency sponsored the present study with the following general objectives.

- Review historical trends in SO_x emissions, particulate emissions, NO_x emissions, and acid rain.
- Review information on size and composition of particulate emissions to identify catalytically active components in the particulates.
- Analyze chemical interactions between particulates and sulfur-bearing gases from coal-fired power plants.
- Predict the impact of the above items on acid rain production.

An extensive review and analysis of available literature was conducted to provide data needed to achieve the preceding objectives. The following sections of this report address the salient observations related to each objective.

HISTORICAL TRENDS IN EMISSIONS AND ACID RAIN

The initial effort involved a review of the trends and/or relationships between emissions and acid rain. The results of this activity are highlighted next.

MASS EMISSION TRENDS

Industrial emissions are estimated on an annual basis by the Environmental Protection Agency (EPA) for inclusion in the Council on Environmental Quality (CEQ) annual report on environmental quality. The first annual report was issued in August 1970 and included emissions estimates for 1968.[1/] Every 5 years, EPA also publishes a detailed national emissions report based on data from the NEDS (National Emissions Data System).[2/]

The emission estimates and trends for sulfur oxides (SO_x) emissions from power plants and from all sources are indicated in Figure 1. The estimates and trends for particulates and nitrogen oxides (NO_x) are indicated in Figures 2 and 3, respectively. The estimates and trends in the 1970's indicate a possible peaking and decline in SO_x emissions. The particulate and NO_x emissions may increase or decrease depending upon emissions control and fuel allocation. In the 1968 to 1974 period, many industries and electrical utilities switched from coal combustion to low-sulfur fuel oil to decrease SO_x and particulate emissions. This move, although decreasing emissions, affects the national energy policy since the United States' supply of low-sulfur oil is restricted compared to the large reserve of coal. In the next few years, until coal gasification or liquefaction is practiced on a large scale, many of these plants will be required to revert to coal for fuel with a potential for increase in emissions levels.

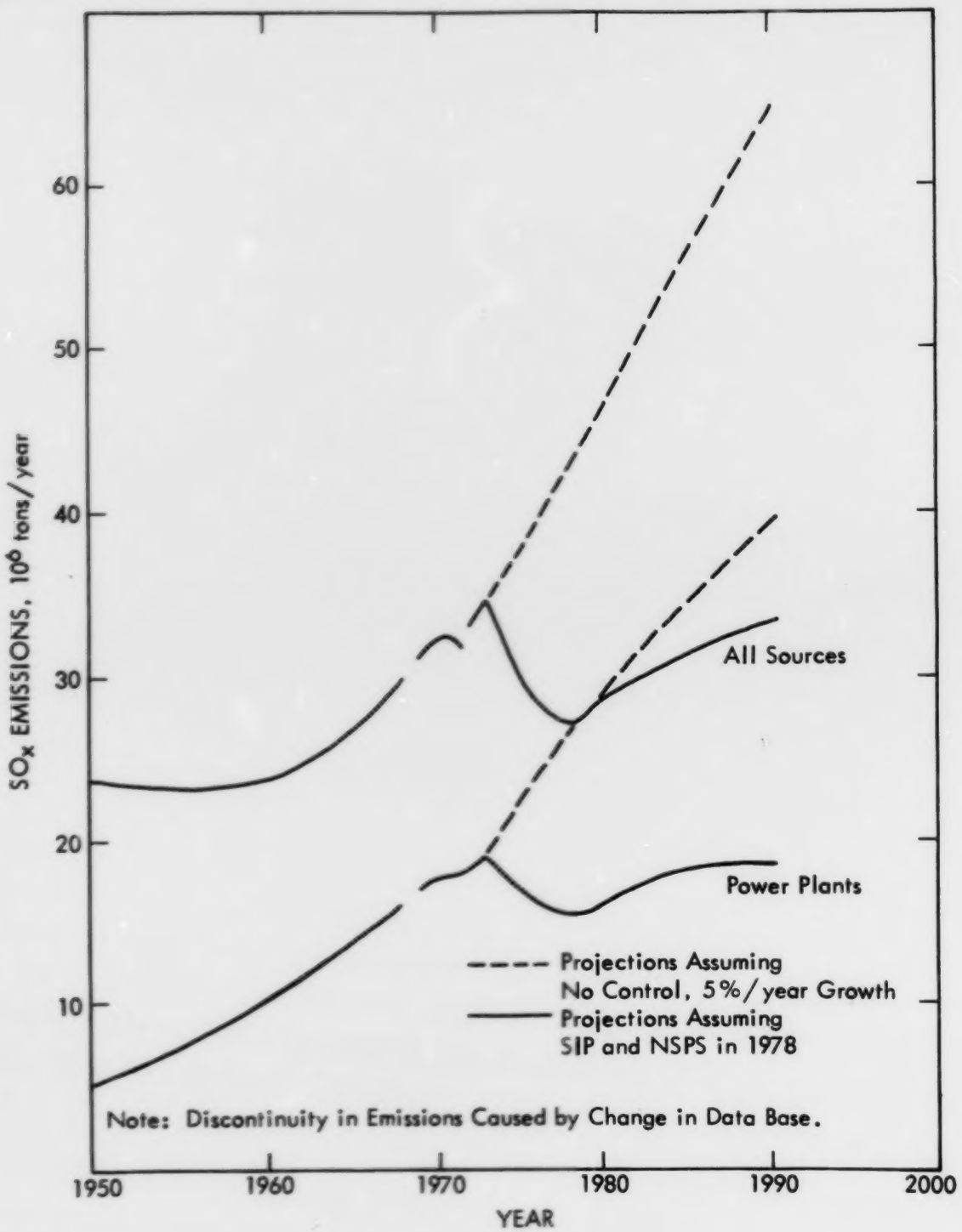

Figure 1. Projected nationwide sulfur oxides emission trends, 1950-1990[2,3]/

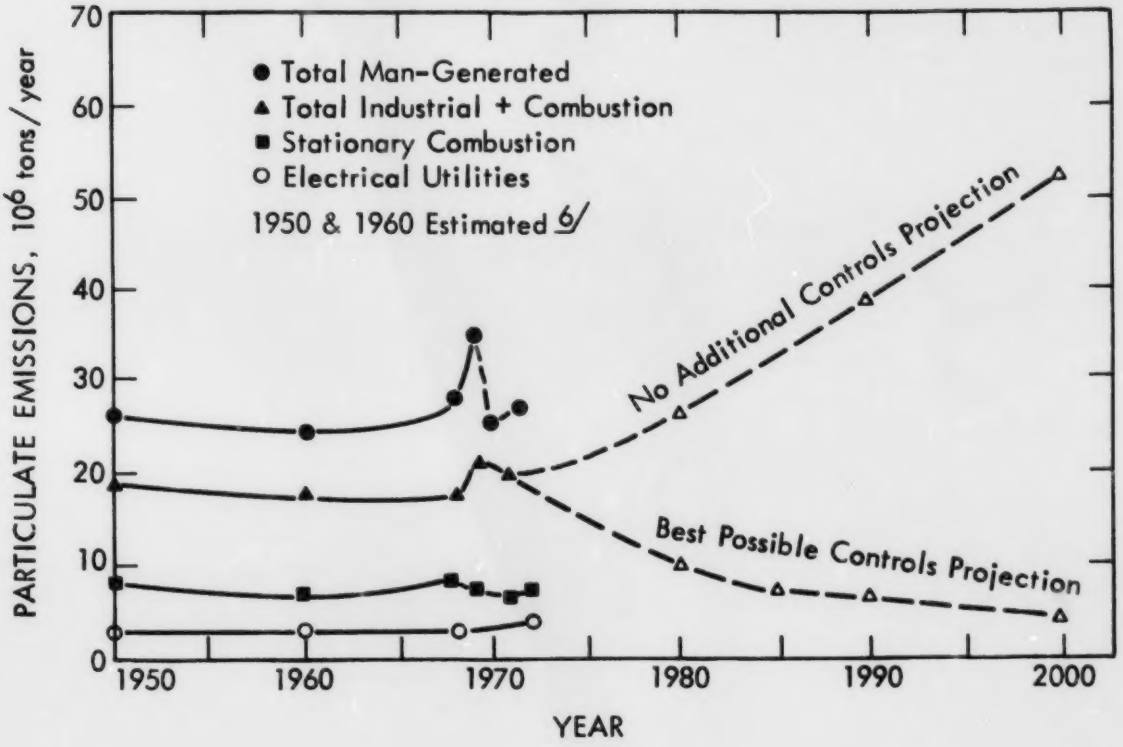

Figure 2. Projected particulate nationwide trends, 1950-1990[1,2,4-6]

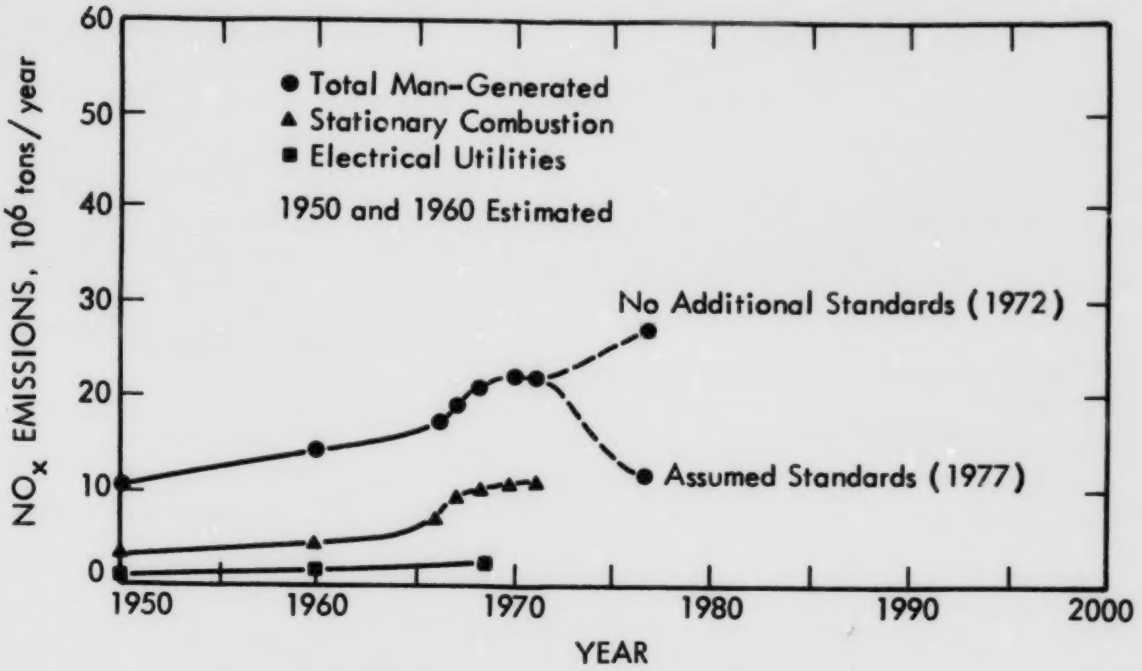

Figure 3. Projected NO_x nationwide trends, 1950-1990[2,5-7]

In considering emission sources which may contribute to the acid rain problem, electric power plants emerge as the major potential contributor. Currently, these power plants contribute 56 to 61% of the SO_x, 11 to 15% of the particulates, and 14% of the NO_x based on data in Figures 1, 2, and 3. In addition, all stationary combustion sources including power plants contribute 73.4% of SO_x, 26% of particulates, and 50% of NO_x.

A backward projection of fossil-fuel combustion process emissions from 1970 to 1920 by Land[8] places these emissions in clearer historical perspective. The SO_x emissions level as indicated in Figure 4 has fluctuated, but was only 26% higher in 1970 than in 1920 and was about the same as in 1942. As indicated in Figure 5, the NO_x emissions level has increased consistently from 1920 to 1970 with the level in 1970 more than three times that calculated for 1920.

The contributions by electric power plants and other stationary combustion sources become even more important when considering the forecasts for electrical energy requirements and the regional pattern of power plant locations and coal utilization. The consumption of coal and the major users are summarized in Table 1 for 1974 through 1976. From this table, power plant consumption of coal is expected to increase by 7.4% between 1975 and 1976 (compared to 3.8% from 1974 to 1975) and the total demand is expected to increase by 7.3% (compared to almost no increase from 1974 to 1975). This increased use of coal may lead to increased particulate and SO_x emissions for 1976 over those projected in Figures 1 and 2. From the coal consumption data in Table 1, power plants are the major consumer and use 70 to 72% of the total domestic demand.

Since fossil-fueled power plants are a major source of the industrial emissions which can cause acid rain conditions, the location of these plants is an important consideration. A map of the United States indicating the location of the major fossil-fueled power plants in operation in 1970 is presented in Figure 6. A high percentage of these power plants are located in the eastern half of the United States. When the prevailing wind directions are considered, this distribution of power plants could lead to a concentration of emissions in the northeastern United States. This area of the United States also includes most of the high-sulfur coal power plants and oil-fired power plants in the U.S., whereas most of the gas-fired plants are located in the Southwest.

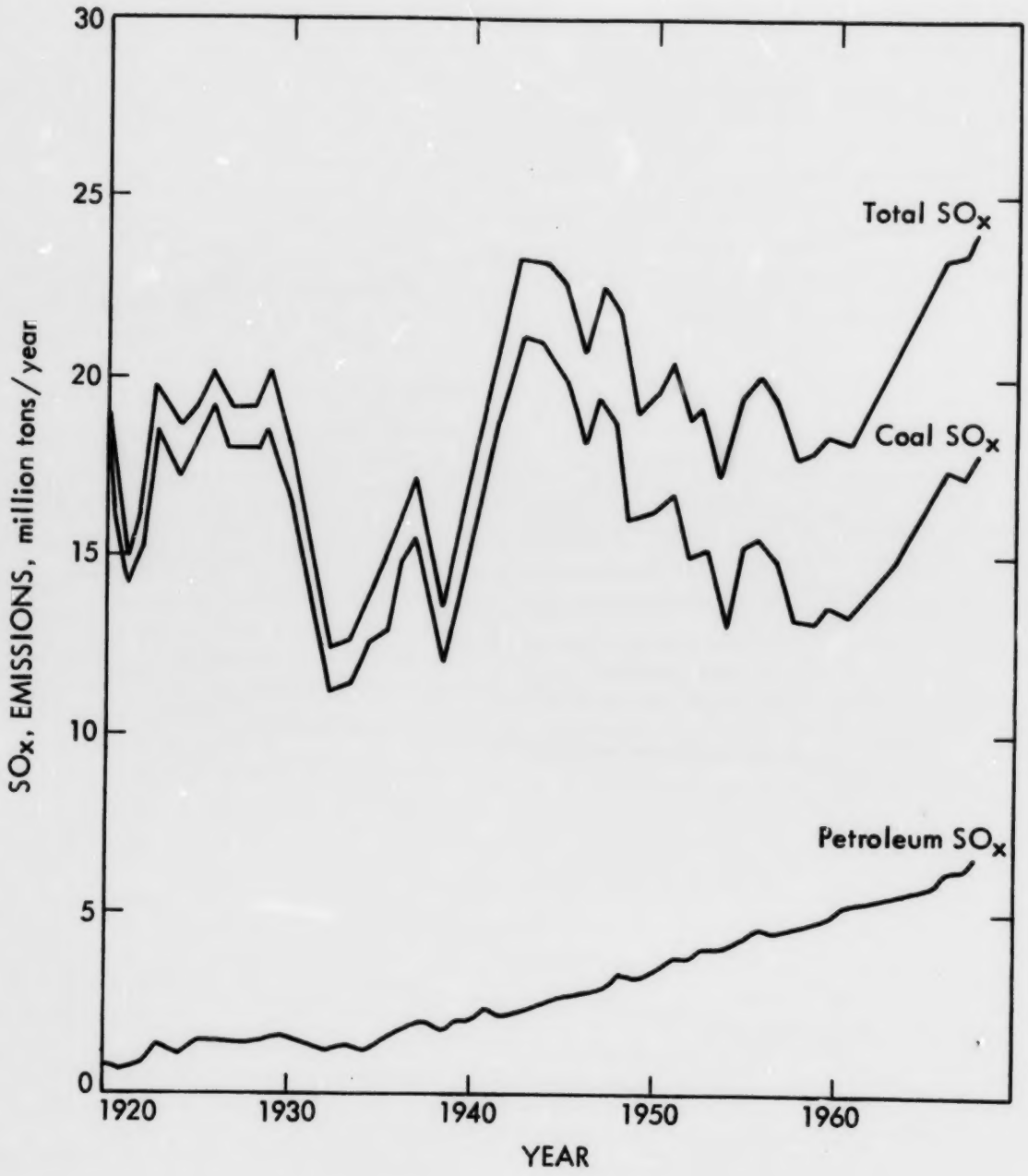

Figure 4. Sulfur oxides emissions from fossil fuel combustion, millions of tons per year[8]

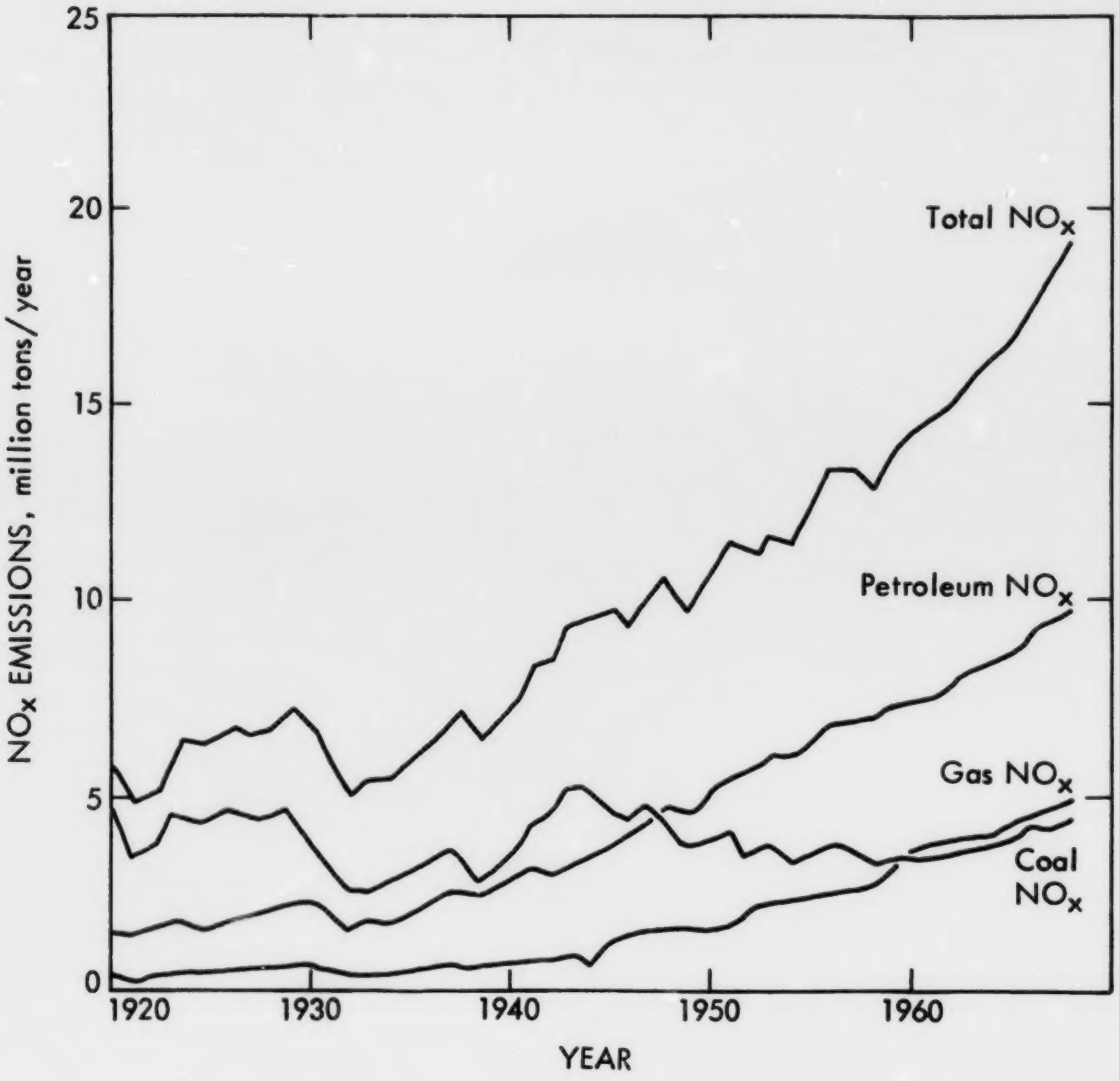

Figure 5. Emissions of nitrogen oxides from fossil fuel combustion, millions of tons per year[8]

Table 1. COAL SUPPLY AND DEMAND (MILLIONS OF TONS)

User	Year 1974[9]	1975[10]	Estimated 1976[10]	Percentage change
Electric utility	390	405	435	+ 7.4
Coking coal	91	83	90	+ 8.4
General industry	70	64	68	+ 6.3
Retail	9	7	7	0
Total domestic demand	560	559	600	+ 7.3
Coal exports	60	65	69	+ 6.2
Total demand	620	624	669	+ 7.2
Total production	590	638	664	+ 4.1

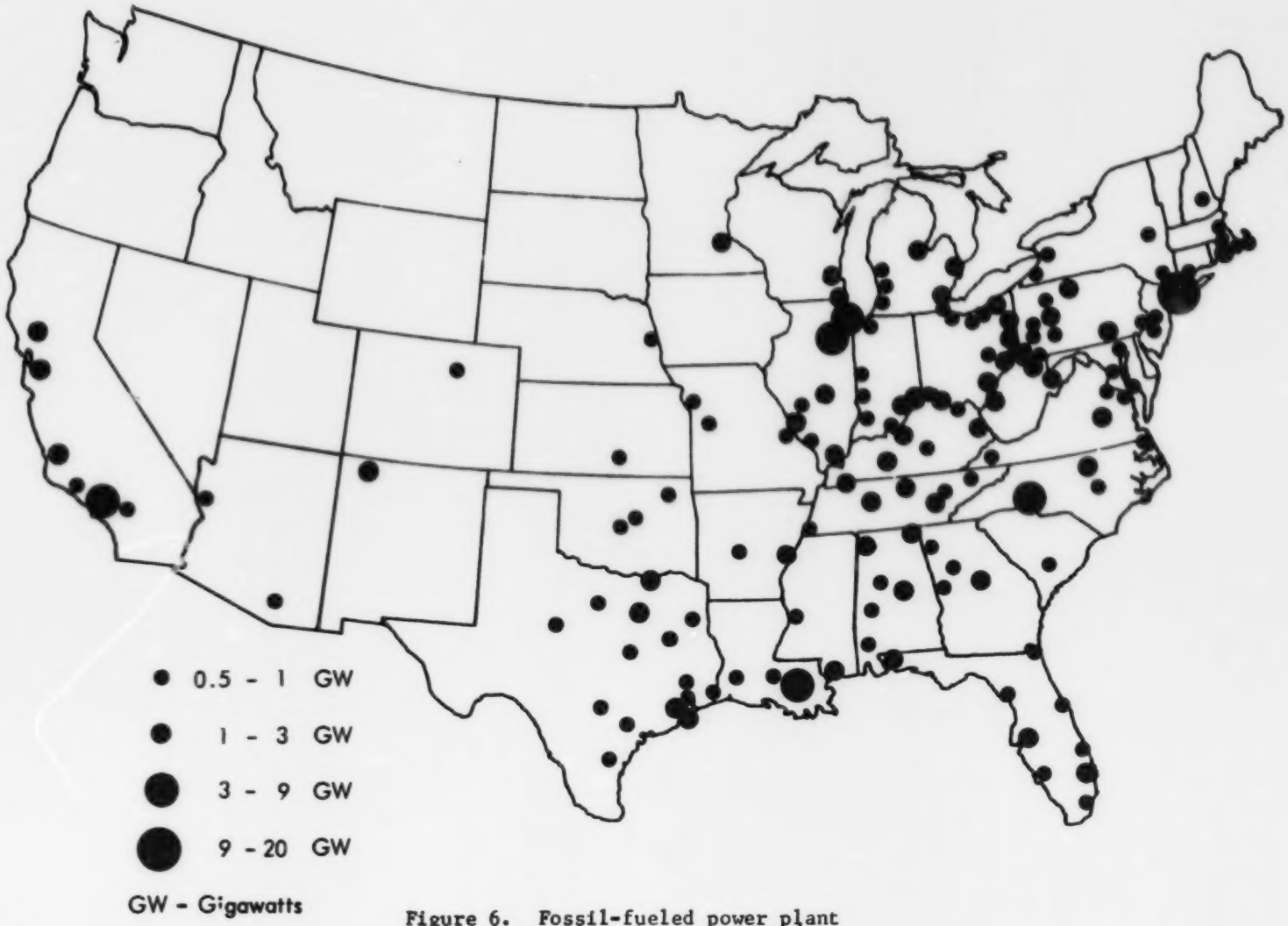

Figure 6. Fossil-fueled power plant generating capacity, 1970[17]

The concentration of SO_2 emissions in the Northeast has been verified as indicated in Figure 7.[13] The estimated SO_x industrial emissions trend for a 24-state region shown in Figure 8 indicates relatively constant emissions of about 22.5 million tons per year from 1970 to 1985.[12] This amount of SO_x emissions represents 70% of the total U.S. industrial SO_x emissions for 1970.

Particulate emissions in the 24-state region totaled 11,013,794 tons in 1972 when the total particulate emissions in the U.S. were 19,789,748 tons.[2] Particulate emissions from electric utilities alone in the 24-state region totaled 2,287,048 tons. This emission level represents 68% of the total U.S. particulate emission from electric utilities.[2] It is clear from these values that the 24-state region of the United States identified in Figure 8 has a higher burden of both particulates and sulfur oxides in terms of mass emissions per year.

AMBIENT POLLUTANT LEVELS AND TRENDS

Mass emissions from industrial sources in specific geographical regions are an indicator of possible pollution problems in a region or city of the United States. More detailed evaluations of the air pollution levels and trends nationally and in regions or cities is made by direct measurement of the ambient pollutants by networks of air monitoring stations. These networks are operated throughout the United States by cities, regions, and states. The U.S. EPA systems, including the National Air Sampling Network (NASN) system and the Regional Air Pollution Study (RAPS), as well as the World Meteorological Organization network are a few examples of such network systems.

Measured levels and trends of ambient levels of sulfur dioxide and sulfates for selected urban and nonurban sites are summarized in Table 2.[12] These data show a significant increase in sulfates in three nonurban sites. The trend comparing 1964 to 1966 and 1970 to 1973 averages for most northeastern urban sites as noted are downward for both sulfur dioxide and sulfates. The composite trends for sulfur dioxide and sulfates are presented in Figures 9 and 10, respectively. The composite SO_2 ambient levels show a cyclic seasonal variation with a slight decreasing trend in maximum and minimum levels. The composite mean urban sulfate levels are almost constant from 1964 through 1970.

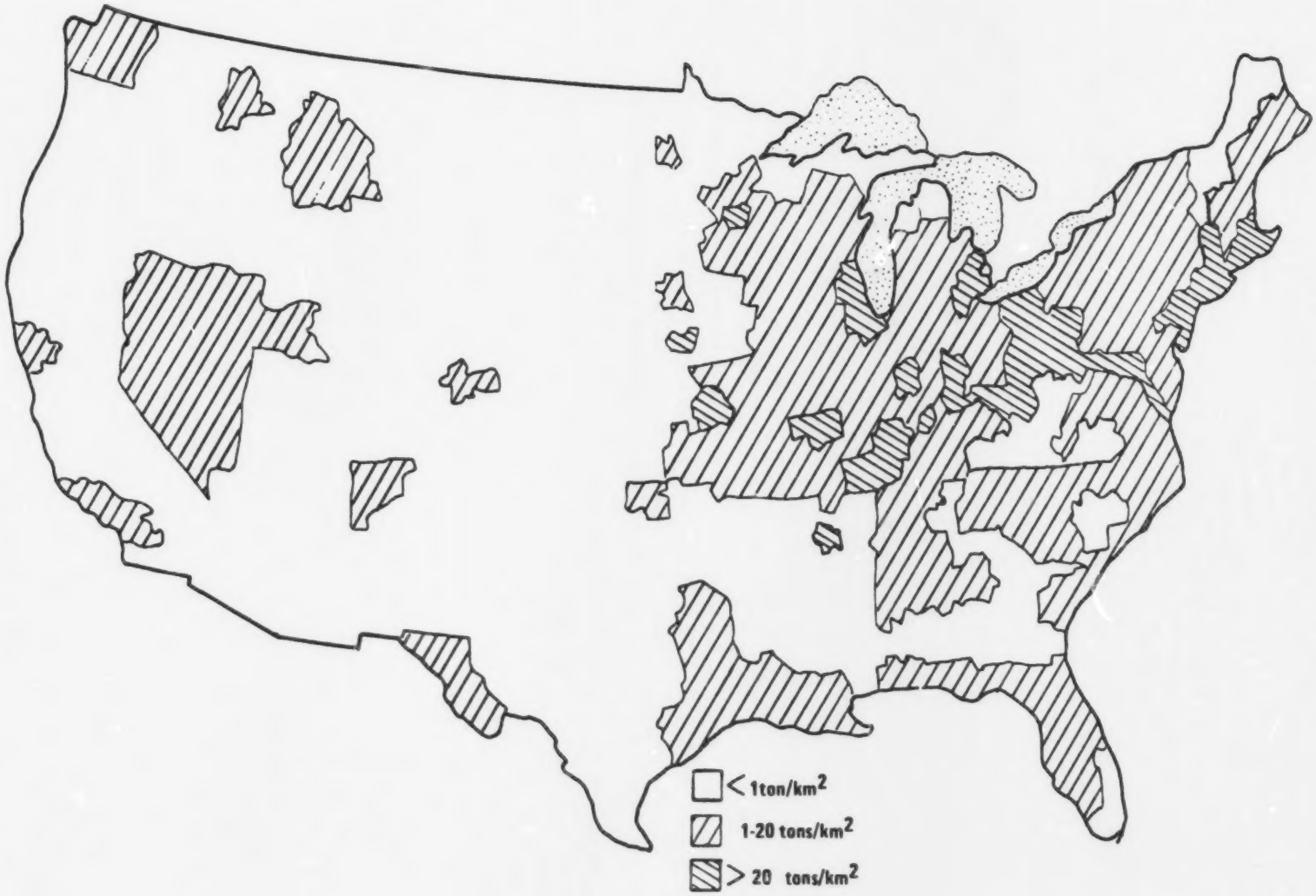

Figure 7. Nationwide geographic variation in annual SO_2 emission density[13/]

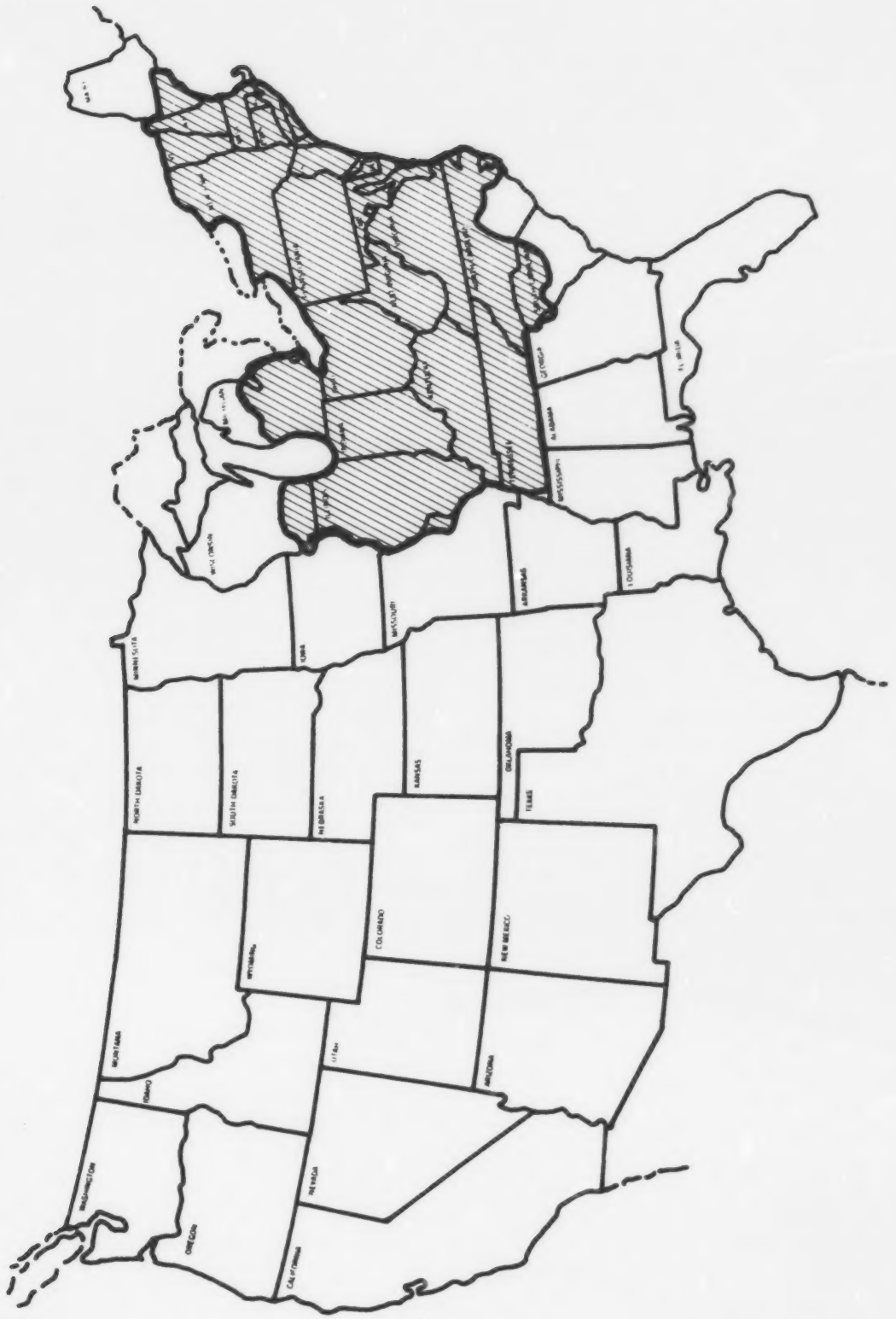

Figure 8. 24-State region with high SO_x emission

Table 2. COMPARISON OF SULFUR DIOXIDE AND SULFATE TRENDS FOR SELECTED URBAN AND NONURBAN SITES[12/]

Site locations*	SO_2, $\mu g/m^3$			Sulfate, $\mu g/m^3$		
	Average, 1964-1966	Average, 1970-1973[a/]	% Change	Average, 1964-1966	Average, 1971-1973[b/]	% Change
Urban sites						
New York, New York	411[c/]	45[c/]	-89.1	26.9	18.5[c/]	-31.2
Glassboro, New Jersey	NA[d/]	14[c/]	-	9.3	11.0[c/]	+18.3
Jersey City, New Jersey	NA	29[e/]	-	22.2[c/]	15.8[c/]	-28.8
Newark, New Jersey	174	8[e/]	-95.4	16.4	13.4[c/]	-18.3
Philadelphia, Pennsylvania	NA	64[c/]	-	23.3	14.9	-36.1
Charleston, West Virginia	21[c/]	15[e/]	-28.6	25.6	17.9	-30.1
Pittsburgh, Pennsylvania	90	56	-37.8	14.3	19.4	+35.4
Youngstown, Ohio	62	28	-54.8	13.3	15.4	+15.8
Cincinnati, Ohio	NA	26	-	13.7	11.7	-14.6
Toledo, Ohio	NA	13	-	12.0	13.5	+12.5
Detroit, Michigan	13[c/]	30	+130	15.3	14.7	- 3.9
Indianapolis, Indiana	57[c/]	20	-64.9	14.0	12.1	-13.6
East Chicago, Indiana	105[e/]	58[c/]	-44.8	17.7	19.1	+ 7.9
Chicago, Illinois	NA	79	-	15.5	15.4	- 0.6
St. Louis, Missouri	86[e/]	32	-62.8	15.6	13.5	-13.5
Nonurban sites						
Shenandoah National Park, Virginia	NA	NA	-	5.9[c/]	9.2	+55.9
Clarion Company, Pennsylvania	NA	NA	-	8.3[c/]	11.0	+32.5
Parke Company, Indiana	NA	NA	-	8.0[c/]	13.6	+70.0

a/ Sulfur dioxide averages are computed for 3 years within the 4-year time span. Qualitative trends "are defined over several sub-intervals and are based on statistically significant changes in geometric mean concentrations."

b/ Some 1-year averages do not include enough samples to meet usual criteria for a valid sampling year. Their use for calculating 3-year means is not a significant problem.

c/ Two-year average.

d/ NA = no data available.

e/ One-year average.

* Adapted from Reference 12, including only those urban/nonurban sites within the 24-state area described in Figure 8.

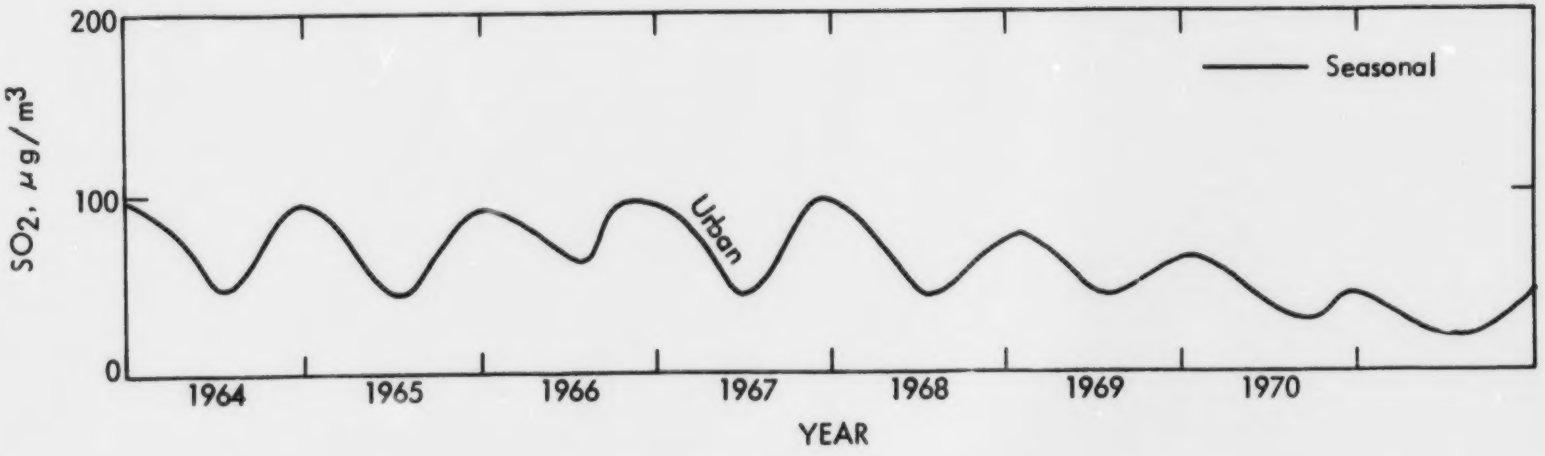

Figure 9. NASN urban sulfur dioxide trends

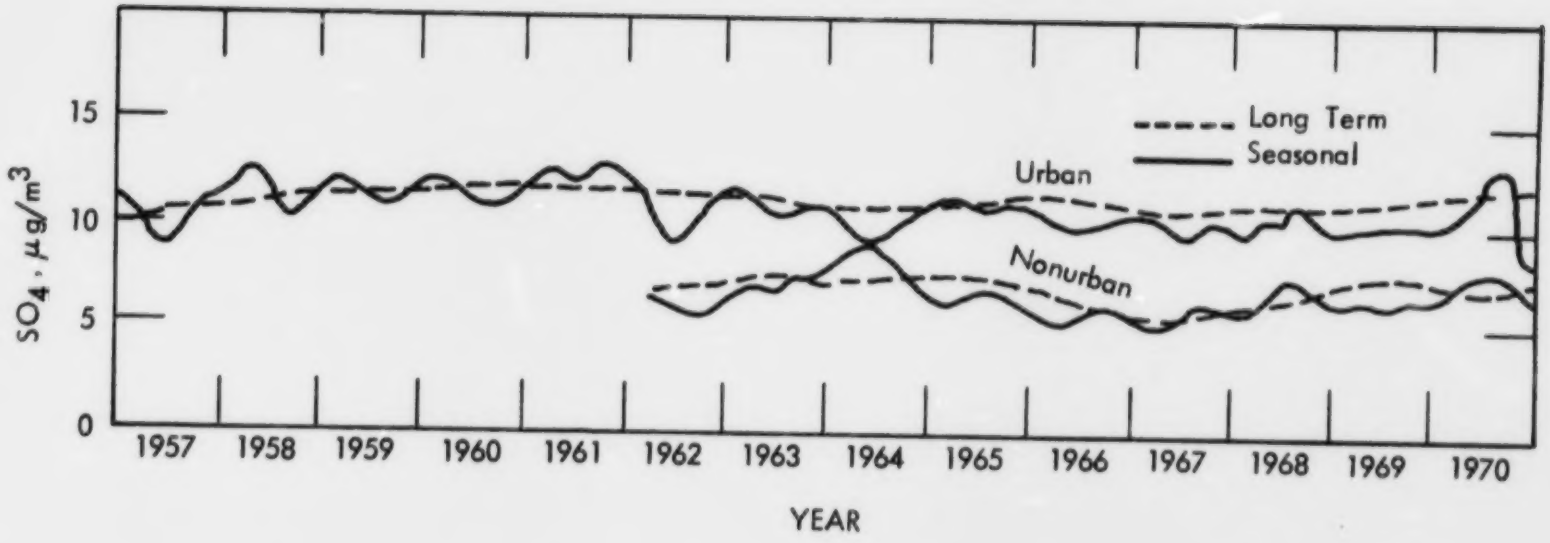

Figure 10. NASN urban and nonurban sulfate trends

The ambient sulfate concentration levels for 1970 are mapped for the United States urban areas in Figure 11 and for nonurban areas in Figure 12. Both of these maps clearly show that higher concentration levels exist predominately in the northeastern region of the United States. A composite mean of the nonurban ambient sulfate levels for the Northeast in Figure 13 shows a significant increasing trend from 6.5 $\mu g/m^3$ in 1965 to 10 $\mu g/m^3$ in 1972 as opposed to the nationwide trend shown in Figure 10.

Other ambient pollutants which may contribute to acid rain formation include nitrogen oxides and the metallic oxides in emitted particulates. Measured data for NO_2 are presented in Figure 14 and give an indication of the magnitude of the NO_2 ambient level and trend. The data in Figure 14 are composite values of NO_2 for seven cities in the northeastern United States and are based on tabulated data published from measurements at the National Air Sampling Network sites for 1967 through 1969.[14] Due to inherent limitations in the measurement techniques used at that time, data should be used with caution. The mean data and maximum and minimum range values as presented in Figure 14 all show a decrease with a mean decrease of 42% in NO_2 24-hr average concentration from 1967 to 1969.

Ambient total suspended particulate concentrations have been reported for the U.S. and for the northeastern region for the 4-year period from 1970 to 1973.[75] These data which are shown in Figure 15 exhibit a decreasing trend, both for the northeastern region as well as the nation. Ambient levels of trace metals have also been measured. Some metals which are present in the atmosphere and their concentrations are listed in Table 3.[15] Unfortunately, trend data for these pollutants are apparently lacking. These metals may be important as catalysts promoting the formation of sulfates and resultant acid rain. One specific element, vanadium, is present due to the combustion of coal and even more from the combustion of fuel oil. Vanadium can play an important role as a catalyst for converting SO_2 to sulfates. Relative amounts of metals present in particulate emissions and their concentration as a function of particle size are discussed in more detail in a subsequent section.

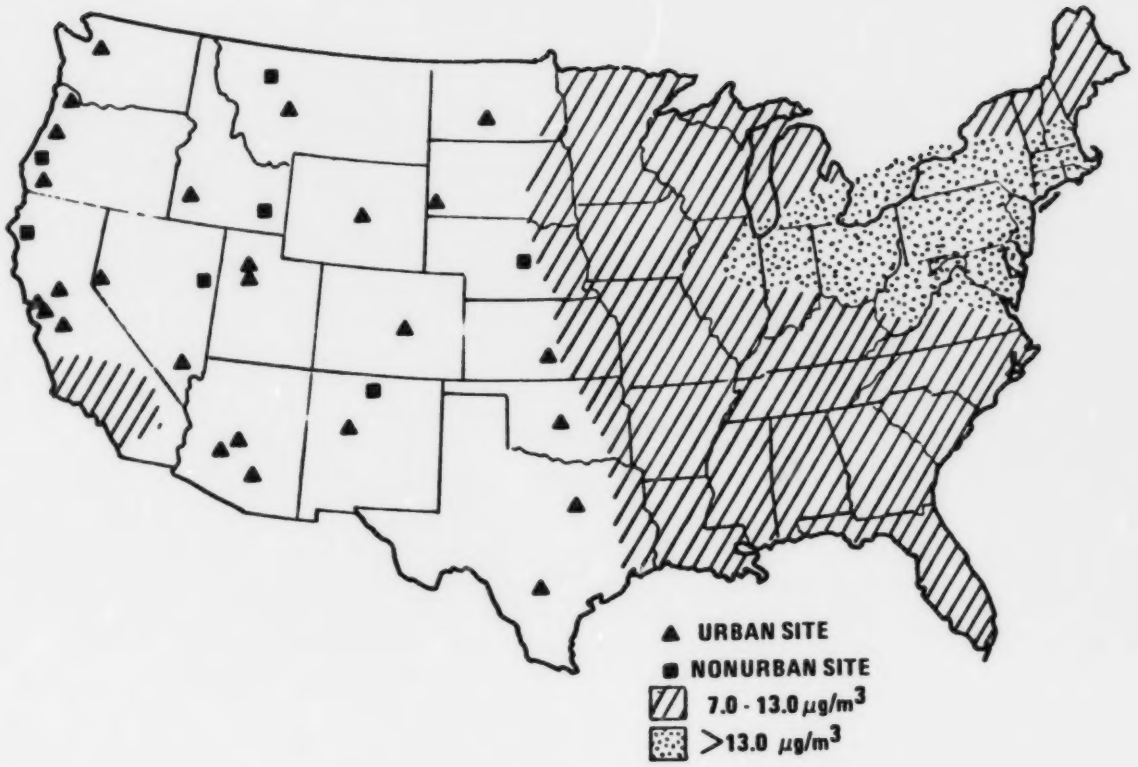

Figure 11. 1970 Annual urban sulfate concentrations[3/]

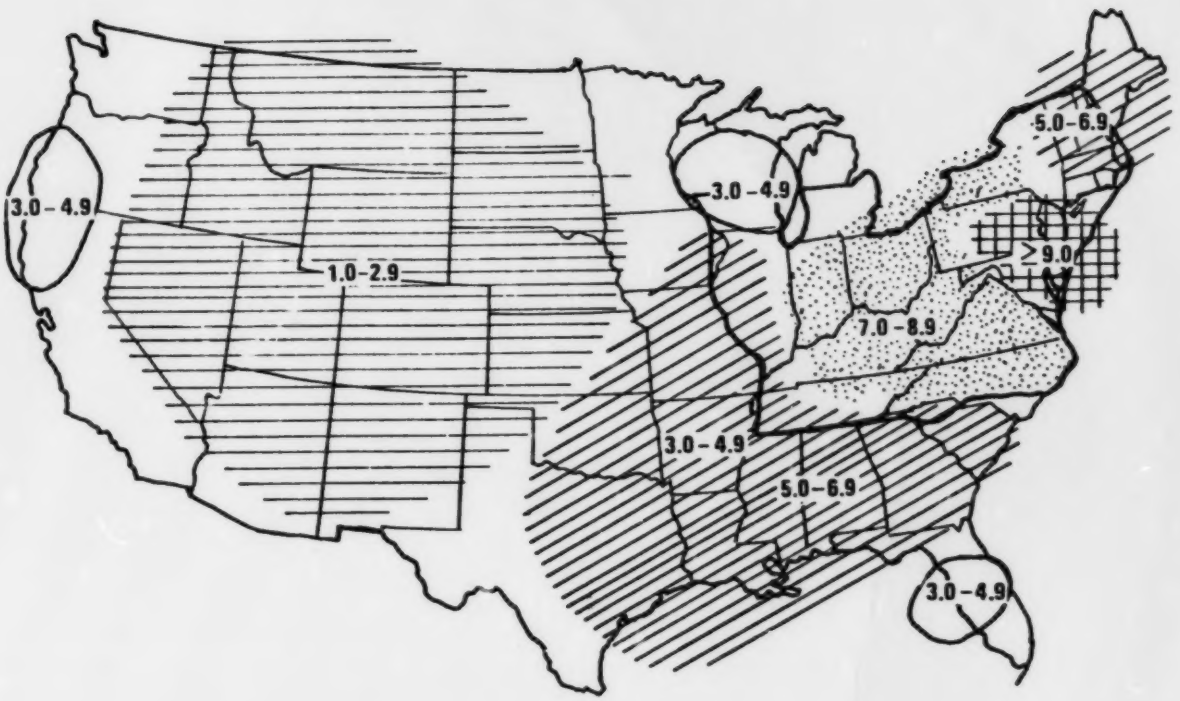

Figure 12. 1970 Annual nonurban average sulfate concentrations[3/]

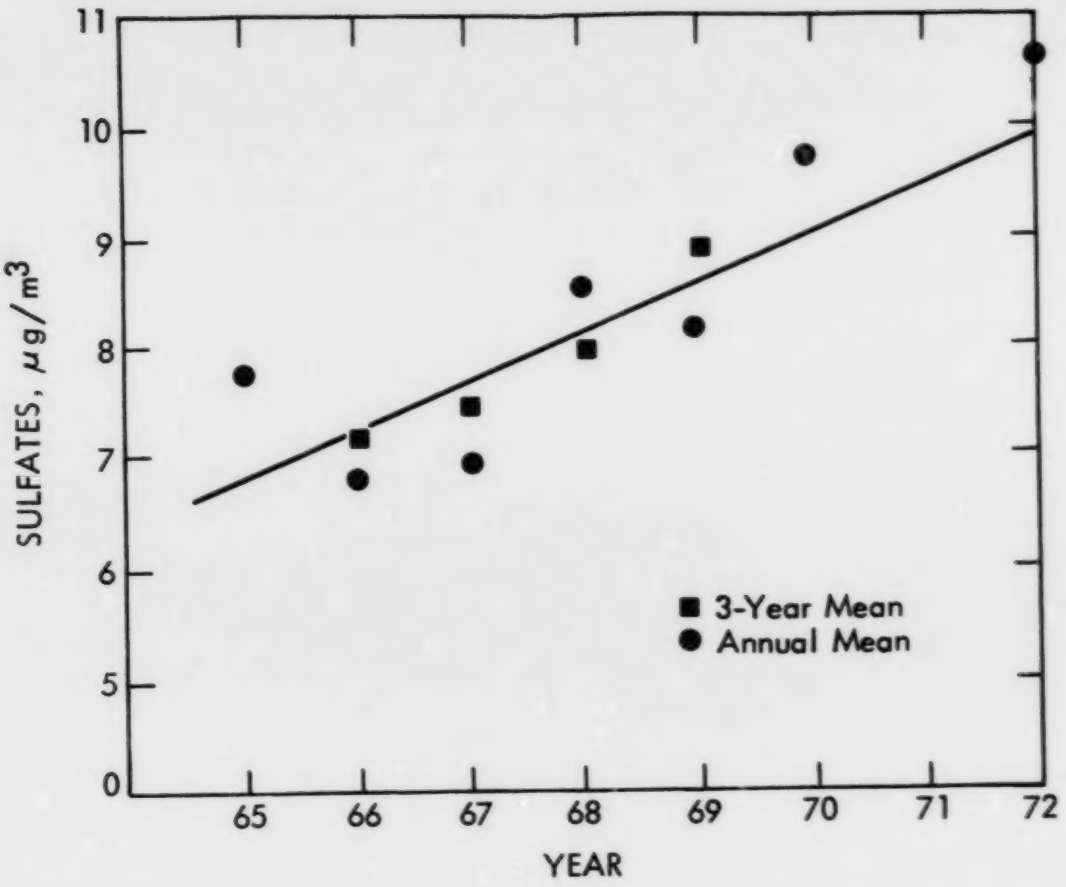

Figure 13. Nonurban sulfate trends in the northeast (8 sites)[12/]

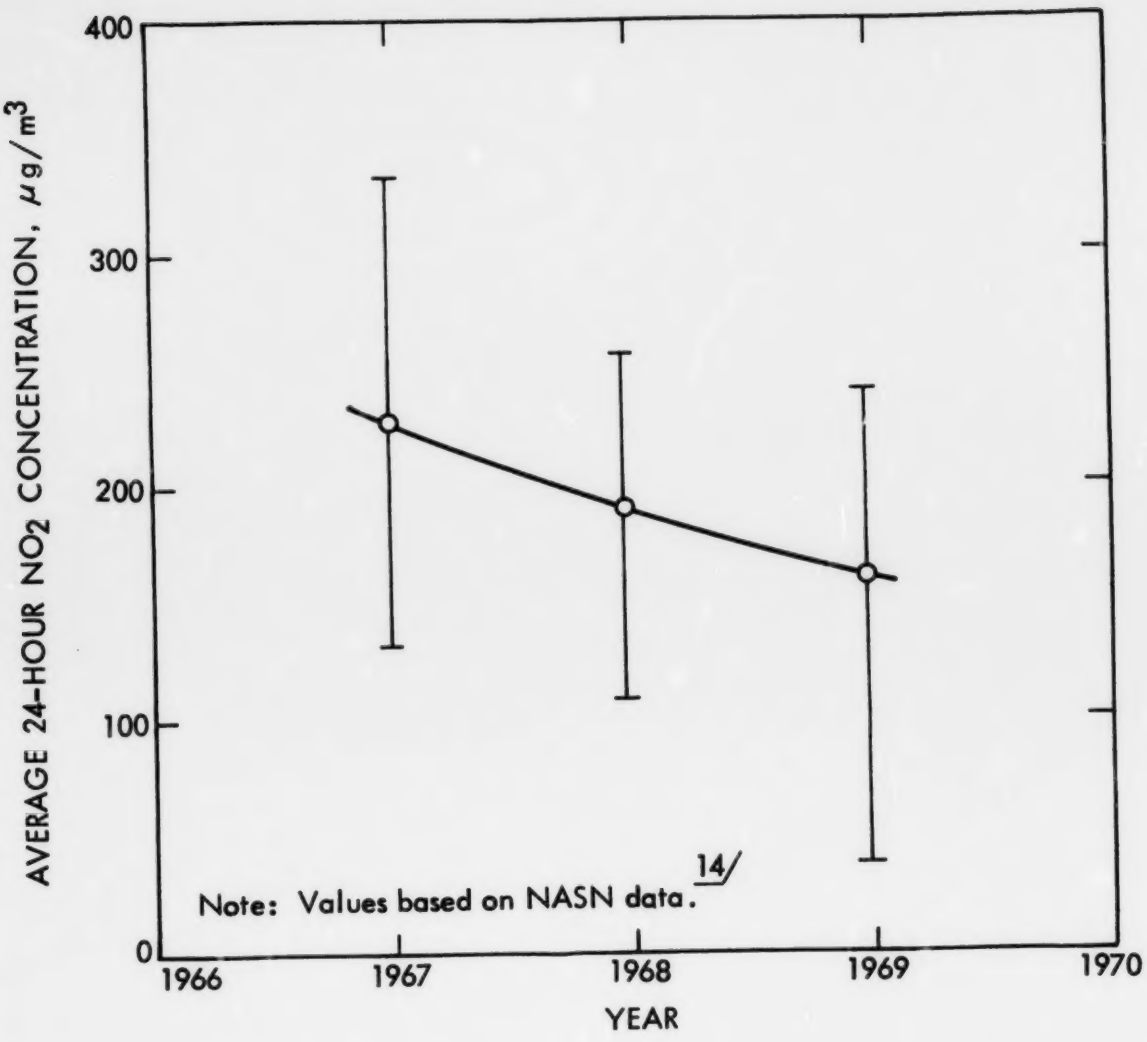

Figure 14. Composite average 24-hr NO_2 ambient concentration for seven northeastern cities, 1967-1969

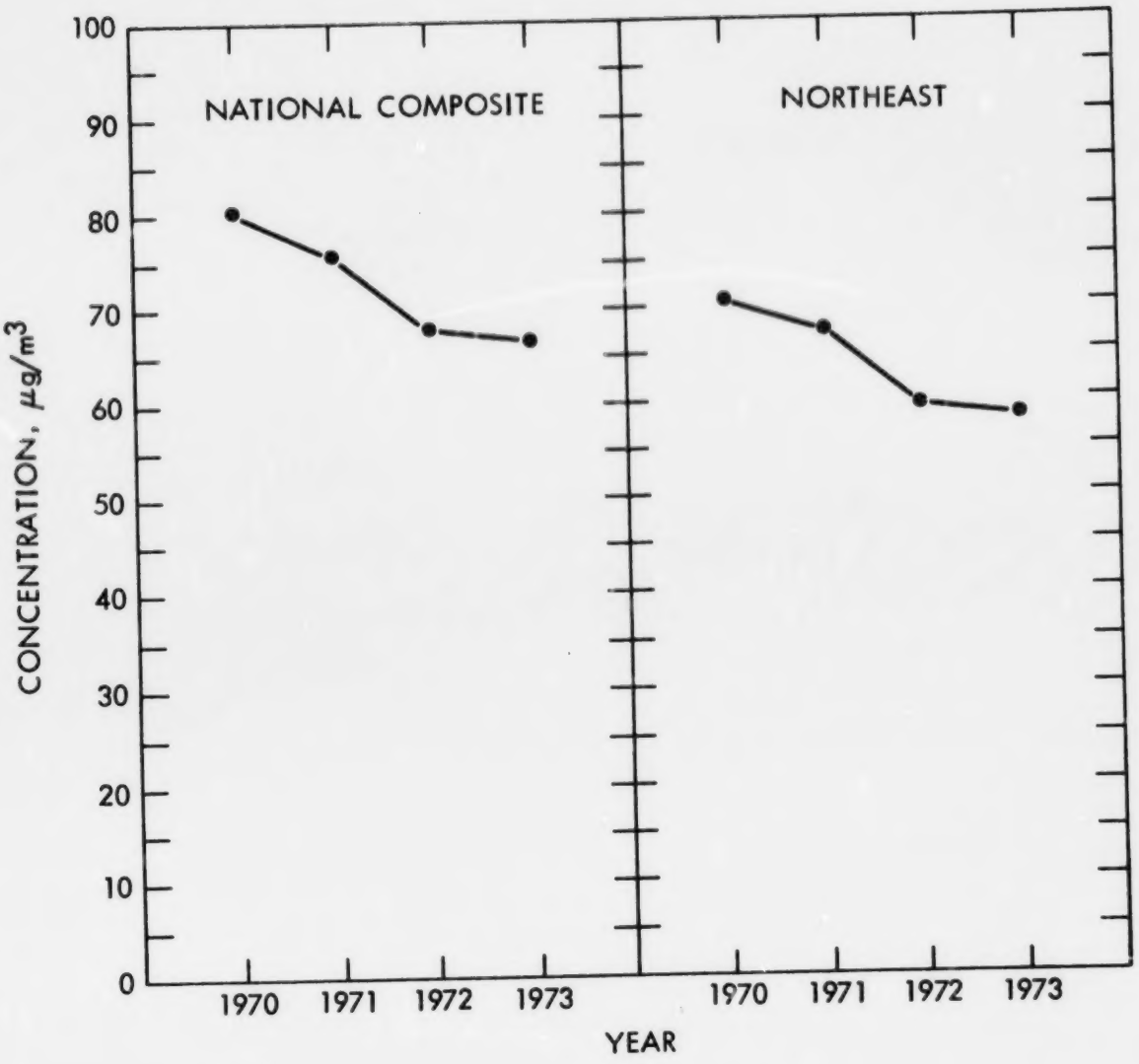

Figure 15. National and northeastern trends for total suspended particulates, 1970-1973[75/]

Table 3. AEROSOL METAL CONCENTRATIONS AT VARIOUS LOCATIONS ($\mu g/m^3$)[15]

Location and year(s) sampled	Ag	Al	Cd	Co	Cu	Mn	Pb	Tl	Zn
Many U.S. urban stations (1964-1965) (4)			2	< 0.5	90	100	790		670
Northwest Indiana, 25 stations (June 11-12, 1969) (5)	< 1-5	1,375-2,600		0.47-2.6	26-4,000	63-390	400-3,700		100-1,540
Columbia, Missouri (1971) (6)		1,520		0.86		30			56
San Francisco, 9 stations (July 23, 1970) (7)	0.05-0.2	250-2,000		0.46-1.7	27-100	5-34			27-500
Corvallis, Oregon, rural (1972) (8)		450		< 0.1	< 35	2.7			
Windward Hawaii (1967) (9)		28			55				
North Atlantic sites (1970-1972) (10)			0.003-0.62		0.12-10		0.10-64		
South Pole (1970) (11)		0.6		0.8	36	10	0.6		30
Chadron, Nebraska (1973)	0.15	535	0.57	3.3	5.3	5.7	45	0.22	16

SUMMARY OF PARTICULATE, SO_2, NO_x TREND DATA

Estimated particulate mass emissions from industrial and combustion sources, on a nationwide basis, appear to have been constant from 1950 to 1968. Beyond 1968, the trend appears to rise until the year 2000, assuming no additional controls. With best possible controls, these emissions show a decreasing trend (see Figure 2). There is a high concentration of particulate mass emissions in the northeastern United States. Data for 1972 indicate that 56% of the total U.S. particulate emissions are emitted in a 24-state region which is to the east of Illinois and to the north of the Tennessee-Mississippi border. However, ambient levels of particulates show a decreasing trend both for the northeast as well as the entire U.S. during the years 1970-1973.

Nationwide, SO_2 mass emissions have been increasing since 1950. This trend is expected to continue until 1990 assuming no additional control and 5% industry growth. However, if new source performance standards (NSPS) and state implementation plans (SIP) become effective in 1978, then there will be a drop in mass emissions before 1980 (see Figure 1). NASN data for urban ambient concentrations of SO_2 show a cyclic but decreasing trend since 1964.

Northeastern United States has a high concentration of SO_2 emissions. Also, the ambient sulfate concentrations are highest for this region both in urban and nonurban areas. However, data for the periods 1964 to 1966 and 1970 to 1973 indicate a downward trend for ambient levels of SO_2 and sulfates for selected urban areas in the Northeast. For nonurban areas in the Northeast, the ambient sulfate concentration has been increasing from about 7 $\mu g/m^3$ in 1968 to 10 $\mu g/m^3$ in 1972.

Trend data for average 24-hr concentrations of NO_2 are apparently limited. During 1967 to 1969 the average concentration has decreased from about 220 $\mu g/m^3$ to about 160 $\mu g/m^3$.

Electric utility plants are predominantly located in the northeastern section of the United States. In 1972, particulate emissions from these plants represented 68% of the total U.S. particulate emissions from electric utilities. Also, this region has limited access to low sulfur coal. Thus if coal-fired power plants continue to be located in the northeast region of the United States, adverse impacts on pollutant trends will occur unless more effective controls are adopted.

ACID RAIN TREND

The acidity of rain has been of concern in Europe since the early 1950's,[16-26] when a network of stations for observing the chemical composition of air and precipitation was established. Analysis of the network data indicate that the main cause for acidification of precipitation in Europe is the increasing use of fossil fuels. It is also reported that large amounts of sulfuric acid can be transported as far as a few thousand kilometers.[26] A more permanent monitoring system is currently being established for measuring ambient air pollutants in Europe under the joint sponsorship of the Economic Commission for Europe--UN, the World Meteorological Organization and the GEMS program of the United Nations Environment Program.[26]

In contrast to the European interest, most of the major efforts in studying acid rain in the U.S. are of a more recent origin.[27-30] Cogbill and Likens report,[31] based on earlier papers on the alkalinity of precipitation in central New York and Tennessee and the acidity of precipitation in Boston, that acid precipitation has been occurring in the northeastern United States as early as 1952. The annual average pH of precipitation for the eastern U.S. during the period 1955 through 1956 is shown in Figure 16.[31] Similarly, using prior chemical data reported for the U.S. during 1960 through 1966, for North Carolina and Virginia during 1962 and 1963 and for New England and New York in 1965 through 1966, Cogbill and Likens have predicted pH of precipitation for the northeastern U.S. during 1965 through 1966.[31] These data are illustrated in Figure 17. Comparison of Figures 16 and 17 indicates the same basic regional distribution of acid precipitation in 1965 through 1966 as that observed 10 years earlier. The distribution for 1965 through 1966 shows an enlarged segment particularly in the northwestern and southern portions of this region. Also, Figure 17 shows intensified acidification in New York and New England. Furthermore, Cogbill and Likens report that the predicted pH for central New York state was 4.44 during 1955 through 1956 compared to a pH of 4.05 in 1973. It is important to note that the predictions made by Cogbill and Likens are based on the existence of a stoichiometric relationship for the major chemical ions in precipitation and a high degree of correlation ($r = 0.96$) exists between their predicted values and actual measurements on rain samples.

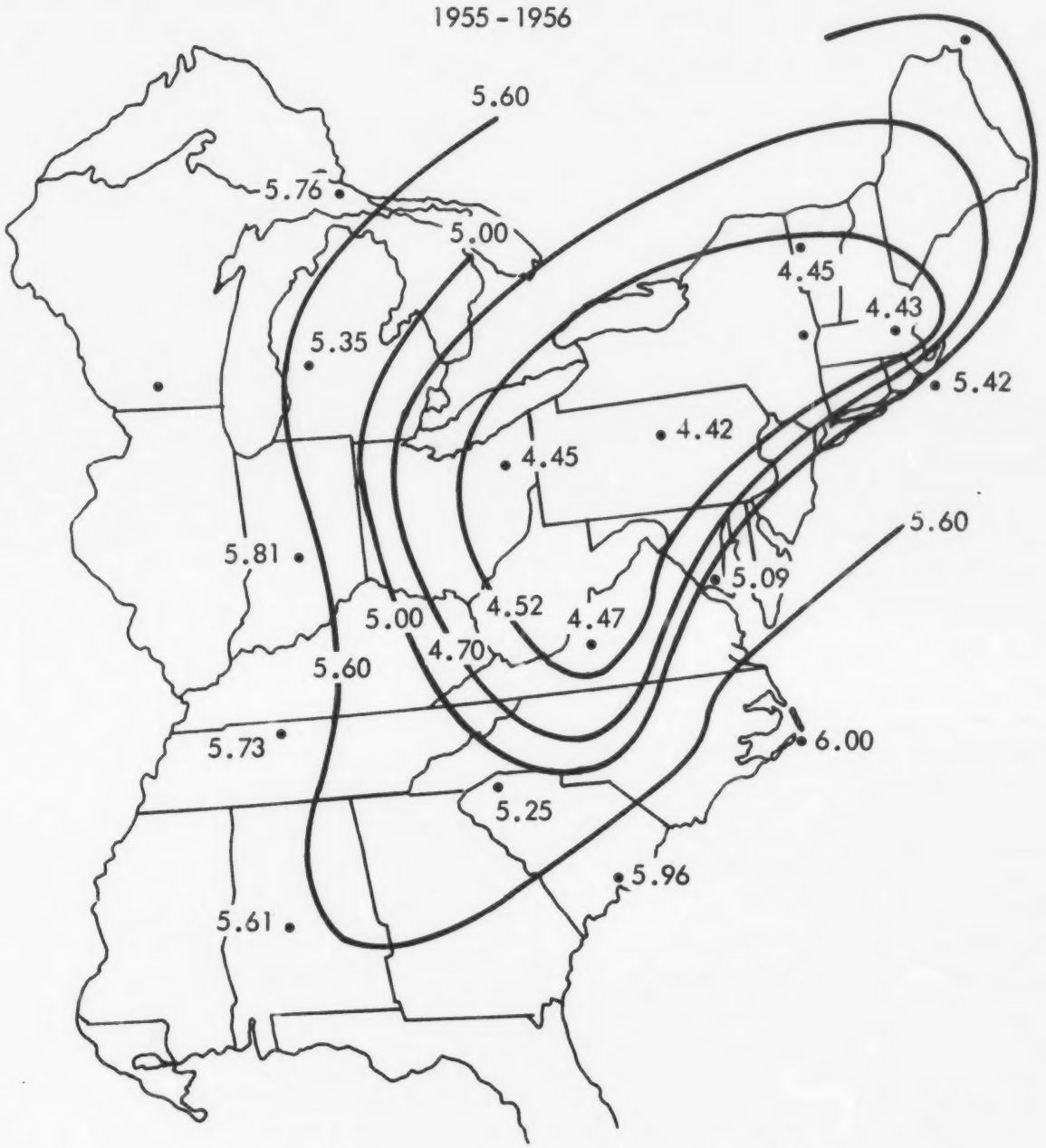

Figure 16. Predicted pH of precipitation over the eastern United States during the period 1955-1956. Isolines are spaced at intervals of 10 microequivalents of H^+ per liter.[31]

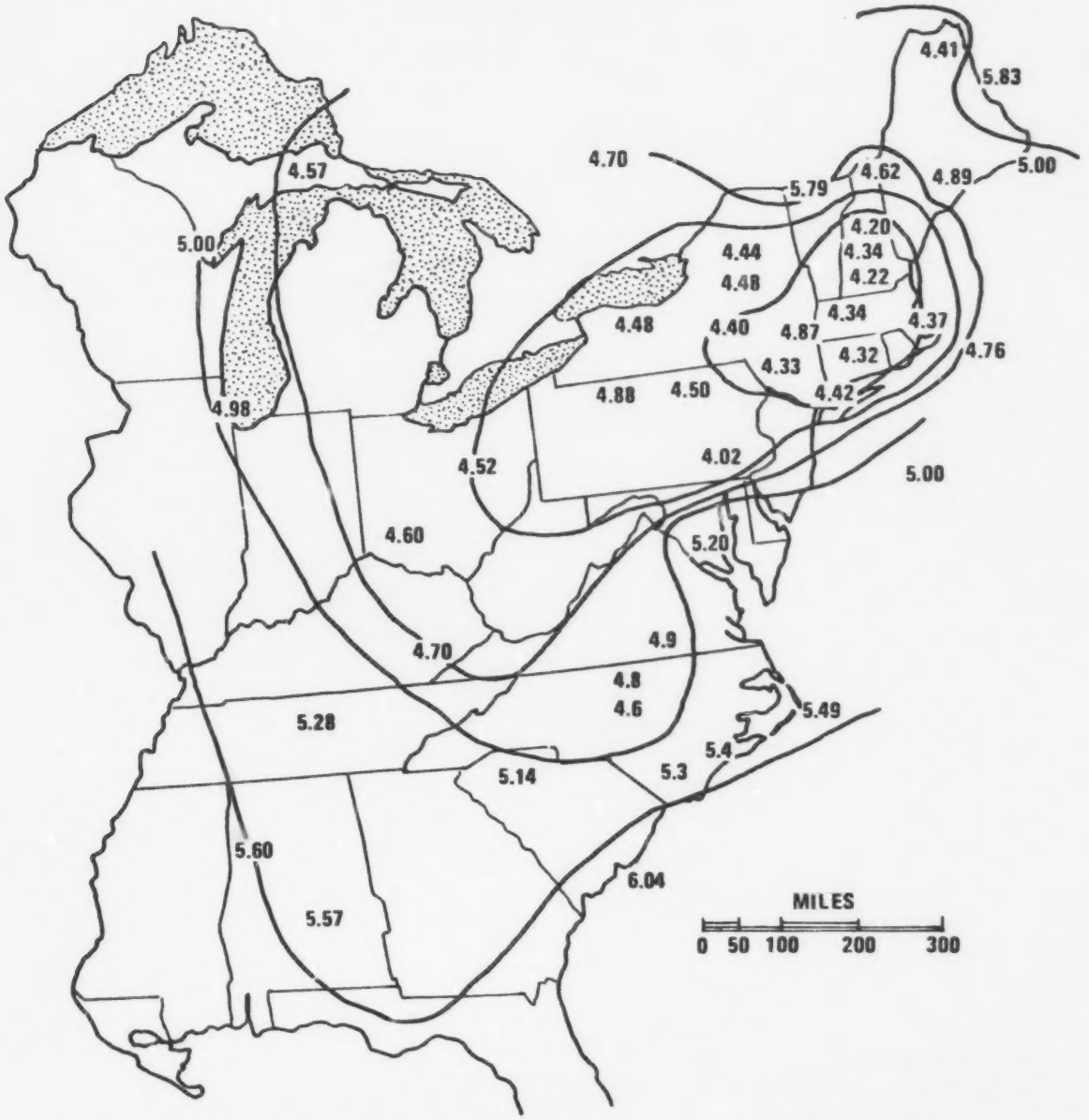

Figure 17. Rainfall acidity, 1965-1966 (pH units)[31/]

Likens and Bormann[30] conclude that precipitation falling in the northeastern United States during the past 11 years is significantly more acidic than elsewhere in the U.S. They report that the annual mean pH of precipitation based upon samples collected weekly during 1970 and 1971 and weighted proportionately to the amount of water and pH during each period of precipitation was 4.03 at the Hubbard Brook Experimental Forest in New Hampshire; 3.98 at Ithaca, New York; 3.91 at Aurora, New York; and 4.02 at Geneva, New York. Also, measurements on individual rain storms frequently showed values between pH 3 and 4 at all of these locations.[30]

The preceding discussion on acid rain trends is based on the limited information that is presently documented. It appears that precipitation in the northeastern United States has become increasingly acidic over the years and further investigation towards a better understanding of the problem, probable causes, and possible solutions is warranted.

SIZE AND COMPOSITION OF PARTICULATE EMISSIONS

It is important to evaluate the size and composition of particulate emissions since they can contribute to the formation of acid rain by acting as catalysts or as adsorption media for SO_3. These mechanisms and their approximate reaction rates are described in the next section. This discussion will primarily address the size and composition of fly ash particulates from coal-fired power plants along with information on trace element concentrations in air.

PARTICLE SIZE DISTRIBUTION

Particle size distributions for emissions from coal-fired power plants are readily available in the literature.[32-35] Figure 18 was obtained from a recent paper and shows the composite mass size distribution of particulates collected before and after an electrostatic precipitator (ESP) at a power plant generating 105 Mw. The stack gas flow rate was 257,000 dry standard cubic feet per minute, equivalent to 7,273 m^3/min. It is clear from Figure 18 that the mass median diameter for the outlet particles is significantly lower than that of the inlet, indicating a higher capture efficiency for the larger particles. Figures 19 and 20 are other sets of particle size data for power plant fly ash obtained at an ESP inlet and outlet, respectively. The presentation of cumulative mass in terms of particulate concentrations in these figures enables calculation of concentrations directly for different particle size ranges. The fractional efficiency curve for the ESP obtained using data from Figures 19 and 20 is shown in Figure 21.

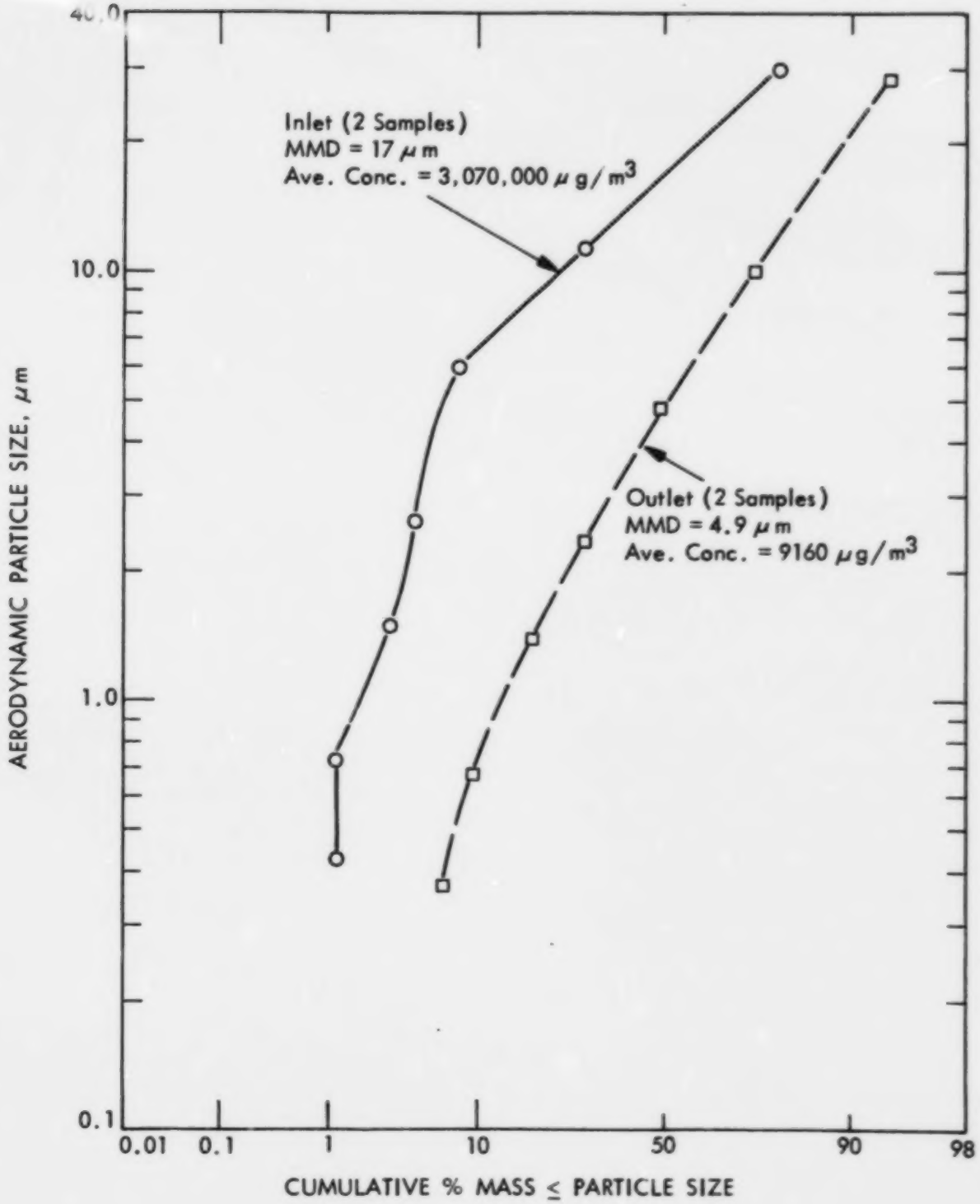

Figure 18. Composite mass size distribution of particulates collected before and after an electrostatic precipitator at coal-fired power plant[36]

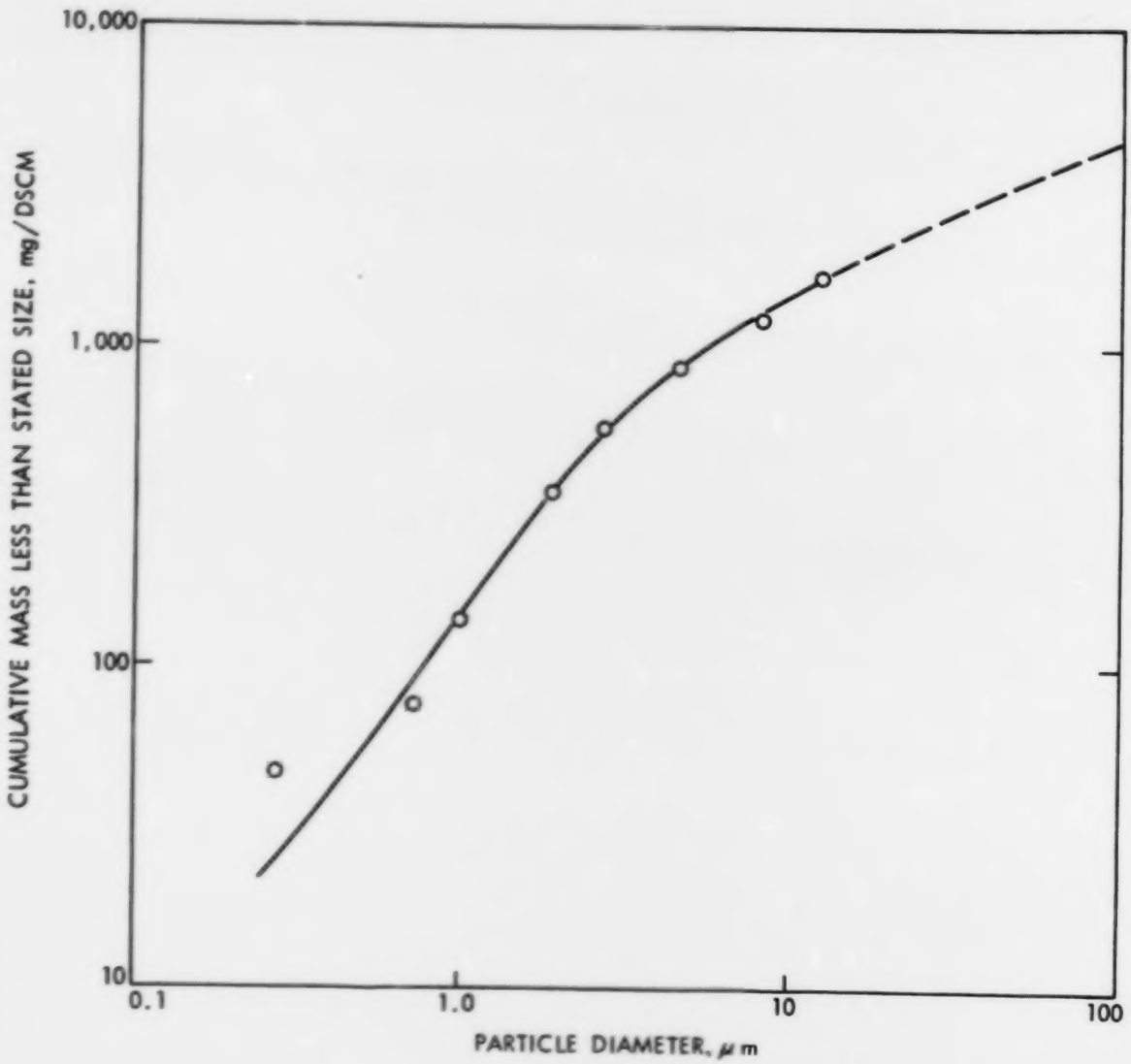

Figure 19. Cumulative particle size data taken at the ESP inlet using Brink Cascade Impactors (average of 27 runs). Particle density = 2.6 gm/cm^3.[37]

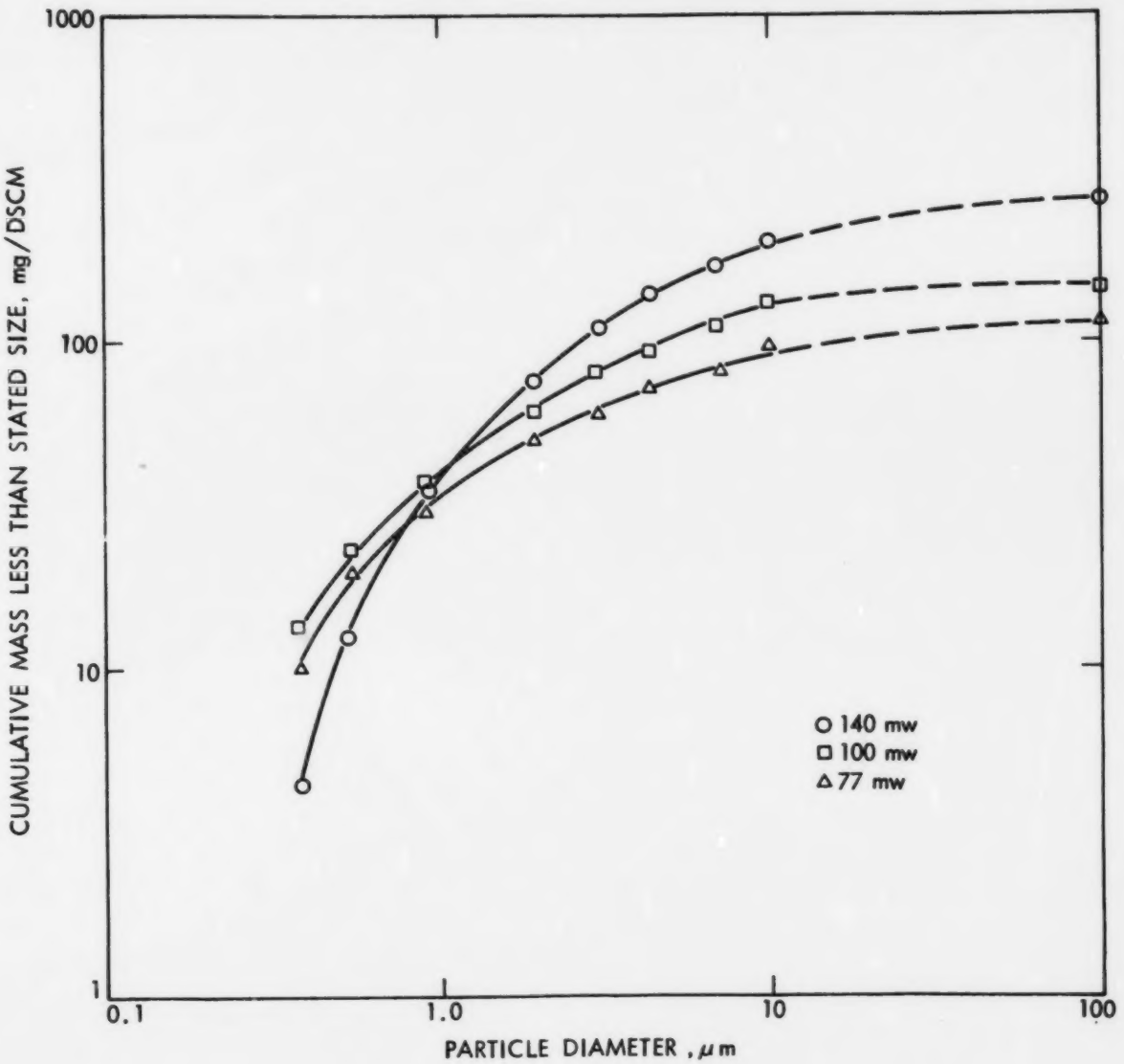

Figure 20. Cumulative particle size distribution taken at the ESP outlet using Andersen Mark III Cascade Impactors. Particle density = 2.6 gm/cm^3.[37]

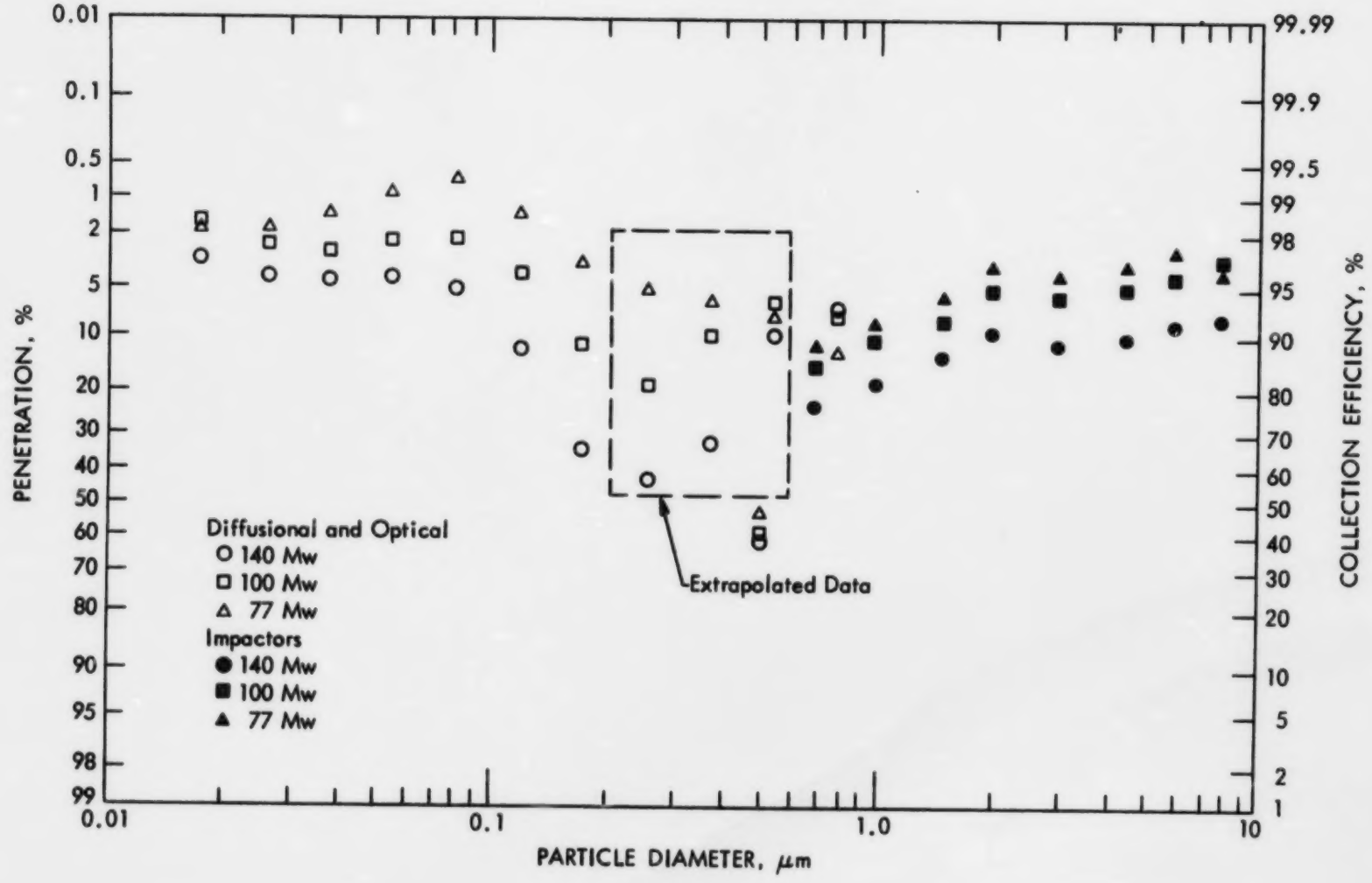

Figure 21. Fractional efficiency of ESP under three boiler load conditions.[37]

Typically, mass collection efficiency is lower for the smaller particles. On a number basis, this means that there are many more smaller particles being emitted to the atmosphere than larger ones. A simple comparison of 1-μm particles with 0.01-μm particles shows that there are 10^6 smaller particles for each 1-μm particle, using the r^3 dependence of n.* This feature is also illustrated in Figure 22, which shows measured outlet particle size distributions for a coal-fired boiler operated at 140 MW. Using the same concept, the ratio of the surface areas has an r^2 dependence. This ratio is 10^4 when the area of a 1-μm particle is compared to another of size 0.01 μm.

The relative proportion of particulates and SO_2 emitted to the atmosphere may also need to be considered since this factor could be important in evaluating their interaction. However, at this point we have not been able to establish the importance of this ratio.

PARTICULATE COMPOSITION

In addition to providing surface area for some of the acid rain forming reactions, particulates also act as catalysts in sulfate forming reactions. Vanadium and cadmium are good examples of catayst contained in particulates which enhance SO_2 conversion. Other metals as oxides including iron, calcium, sodium, magnesium, and lead also react with SO_2 to form metal sulfates. Whether or not these metals play an important role in the formation of acid rain depends on their concentration in the atmosphere and their accessibility within the particles for reaction with the SO_2.

Table 4 shows the major elements observed in analyzing 28 samples of fly ash.[38] Ashes 1 through 15 came from western coals, while ashes 16 through 28 were produced from eastern coals. By far the major constituents are SiO_2, Al_2O_3, CaO, and Fe_2O_3 for western coals and SiO_2, Al_2O_3, and Fe_2O_3 for eastern coals. Due to higher concentrations of CaO and Na_2O, fly ash from western coals is usually more alkaline than eastern coals. The major elements are reported as oxides in weight percent to enable conversion to molecular fractions from which molecular percent oxides and atomic percent cations could be determined.[38]

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* For particles of radius r_o, density ρ, and numbering n_o, the mass is given by $4/3\ \pi r_o^3 \times n_o \times \rho$ and for particles of same density but having radius r_1, the number n_1 is given by:

$$n_1 = \left(\frac{r_o^3}{r_1^3}\right) n_o \quad \text{or} \quad \frac{n_1}{n_o} = \left(\frac{r_o}{r_1}\right)^3$$

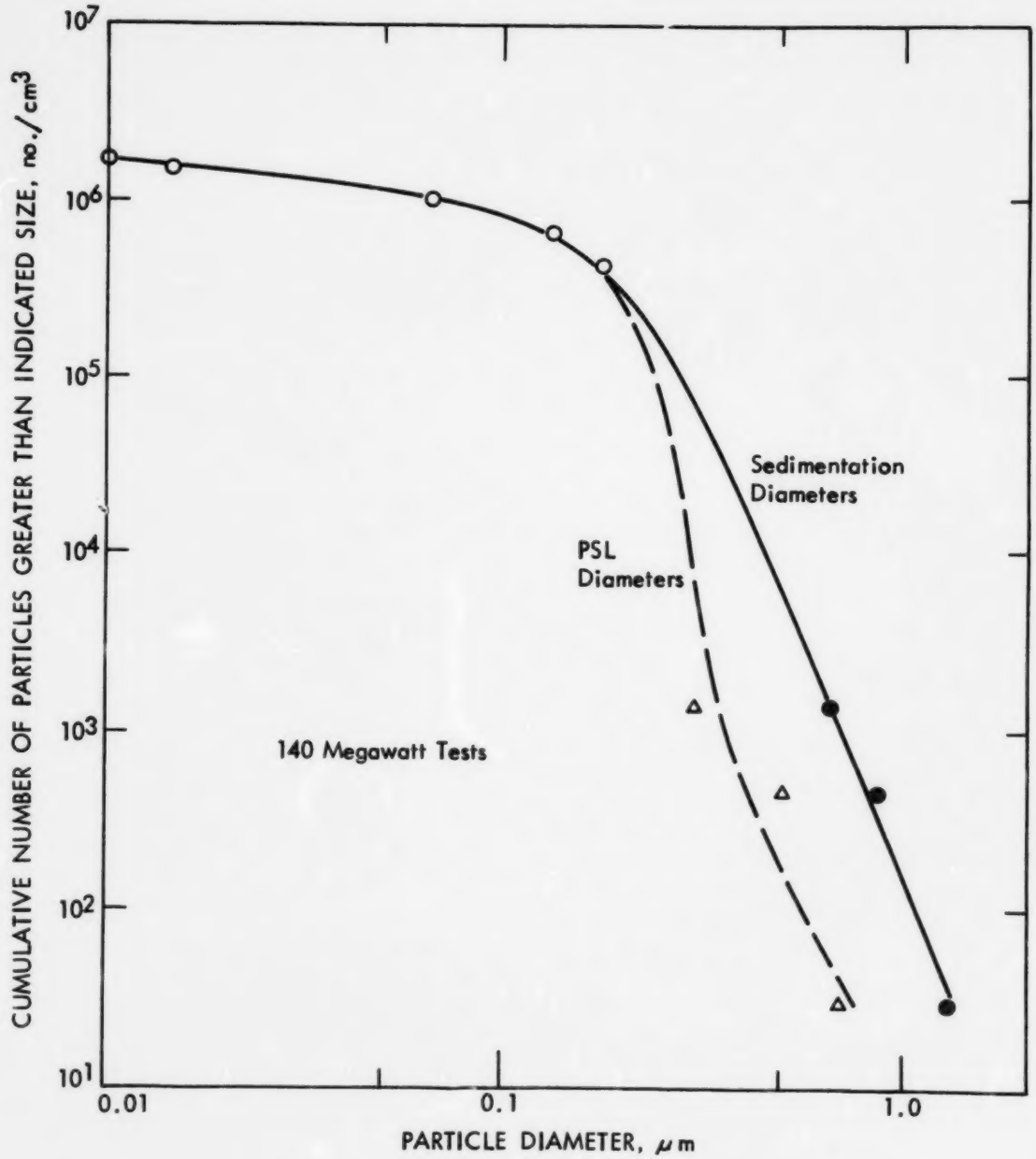

Figure 22. Outlet size distributions (optical and diffusional) at 140 Mw boiler load[37]

Table 4. CHEMICAL ANALYSES OF FLY ASHES[38]

Ash No.[a]	Expressed in weight percent as oxides											
	Li_2O	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	P_2O_5	SO_2[b]	LOI
1	0.04	0.09	0.30	5.40	21.50	4.30	22.80	40.15	1.30	0.34	1.70	0.33
2	0.01	0.24	0.89	3.30	23.50	5.53	21.20	40.50	2.13	0.54	1.83	0.20
3	0.01	0.25	0.89	1.88	11.10	3.71	23.60	55.60	1.56	0.14	0.32	0.74
4	0.01	0.34	0.77	1.60	11.60	3.60	25.30	56.80	0.83	0.17	0.17	0.60
5	0.01	0.32	0.90	1.80	12.70	3.90	25.80	55.00	0.89	0.17	0.32	0.65
6	0.01	0.53	1.10	1.70	12.20	4.20	25.10	55.10	0.83	0.18	0.24	0.60
7	0.02	1.30	0.72	2.50	8.60	4.65	18.20	59.00	2.20	0.19	1.05	0.45
8	0.02	1.07	0.70	2.23	8.30	4.66	17.70	61.00	1.53	0.16	0.77	0.50
9	0.02	1.77	1.13	1.93	6.36	4.61	24.60	53.70	1.49	1.06	0.79	1.49
10	0.01	3.10	0.80	0.90	10.40	3.40	28.20	52.00	0.88	0.18	0.26	0.45
11	0.01	2.10	1.00	0.99	12.30	4.60	26.50	52.00	0.93	0.21	0.36	0.40
12	0.01	2.40	1.00	0.93	13.60	4.80	26.20	49.20	0.93	0.24	0.46	0.45
13	0.02	0.38	2.36	2.59	11.41	6.03	19.64	55.29	0.95	0.60	0.58	0.35
14	0.01	1.47	0.68	1.73	7.33	5.33	23.10	53.10	4.17	0.90	1.11	0.44
15	0.01	1.84	0.20	12.75	31.00	11.20	14.80	22.00	0.60	0.39	4.80	0.41
16	0.05	0.48	2.75	0.88	0.87	5.50	27.80	50.45	1.85	0.23	0.70	7.70
17	0.04	0.49	3.12	1.09	2.48	13.24	26.40	50.70	1.62	0.28	0.57	1.00
18	0.05	0.32	2.30	0.98	4.60	23.70	21.20	42.70	1.40	0.34	0.69	5.50
19	0.02	0.23	2.80	0.86	2.20	23.00	21.00	47.70	1.80	0.52	1.30	21.0
20	0.02	0.51	2.80	0.93	0.26	17.90	21.90	51.00	1.40	0.33	0.96	1.80
21	0.01	0.35	2.36	1.66	3.72	16.10	17.80	43.30	1.27	0.36	0.64	10.30
22	0.04	0.33	3.88	1.57	0.77	10.01	27.50	51.40	1.79	0.32	0.37	1.50
23	0.03	0.38	3.34	1.29	1.04	9.70	25.90	29.90	1.98	0.32	0.42	4.40
24	0.07	0.40	3.10	1.20	1.40	8.80	29.00	52.40	1.70	0.40	0.29	3.20
25	0.05	0.16	2.60	0.93	0.87	8.40	31.00	55.10	2.30	0.36	0.23	1.40
26	0.04	0.51	3.80	1.30	0.68	4.90	30.20	53.00	2.00	0.17	0.36	2.50
27	0.05	1.55	2.80	1.15	2.50	3.85	25.00	56.75	1.55	0.28	1.12	1.70
28	0.06	0.42	3.70	1.30	1.10	9.90	30.30	52.40	1.70	0.51	0.45	1.30

a/ Ash Nos. 1-15 are for western coals and 16-28 are for eastern coals.
b/ Total sulfur in ash.

Several sources report trace element concentrations in fly ash.[39-42] Of these, References 39 and 42 are of special value. Reference 39 indicates trace metals in fly ash as a function of particle size and also their concentration and size in urban air. These are shown in Tables 5 and 6, respectively.

Table 5 shows that particles 1.5 μm in diameter contain greater quantities of cadmium, chromium, manganese, and lead than larger-sized particles. Higher concentrations of iron are associated with particles >1.5 μm. These data indicate preferential concentration of some elements as a function of particle size. Metals which tend to concentrate in the submicron particles can escape capture by most conventional emission control devices which exhibit relatively poor efficiency in this size range. Airborne metals found in concentrations of the order of 1 $\mu g/m^3$ or greater include iron, lead, zinc, magnesium, copper, and vanadium as shown in Table 6. All of these are present in particulate emissions from coal-fired power plants.

A listing of trace element stack emissions from tests at four different coal-fired power plants is shown in Table 7.[42] Values in the table represent fractions in coal, expressed as percent, released to the atmosphere. Values in Column A were calculated from analyses of ashes collected from the unit whereas values in Column B were calculated from analyses of fly ash and flue gas sampled from the stack. A "0" entry signifies that the calculated value was ≤ 0; a "-" entry signifies that a numerical value could not be calculated from the experimental data.[42] Mass balances reported by groups identified with the four separate studies were used in calculating, for each element, the fraction emitted to the atmosphere.[42]

Table 8 presents measured air concentrations of specific elements and compares these values with the upper value of expected concentrations observed in stack emissions from coal-fired systems.[43] Ambient concentrations shown in Table 8 do not take into account elements that may be present in vapor form, and this could result in erroneous comparisons for these elements unless appropriate correction is made.

Table 5. TRACE METALS IN FLY ASH AS A FUNCTION OF PARTICLE SIZE[39]

Element[a]	Concentration, ppm				
	25 μm	12.5 μm	10 μm	3.5 μm	1.5 μm
Al	67,000	54,300	57,300	63,600	59,300
B	300	500	500	500	500
Be	2	1	2	2	2
Cd	≤ 5	≤ 5	≤ 5	≤ 5	100
Cr	130	130	130	300	300
Cu	150	150	200	200	200
Fe	40,000	59,000	43,500	35,500	32,300
Mn	200	240	290	390	500
Ni	300	200	200	300	300
Pb	300	200	300	300	500
V	200	200	300	200	200

a/ Sample collected from a coal-fired steam power plant and analyzed by neutron activation and spark source mass spectrometry.

Table 6. CONCENTRATION AND SIZE OF TRACE METAL PARTICLES IN URBAN AIR[39]

Metal	Concentration ($\mu g/m^3$)	MMD[a] (μm)	Particles < 1 μm (%)
Fe	0.6-1.8	2.35-3.57	12-35
Pb	0.3-3.2	0.2-1.43	59-74
Zn	0.1-1.7	0.58-1.79	14-72
Cu	0.05-0.9	0.87-2.78	16-61
Ni	0.04-0.11	0.83-1.67	28-55
Mn	0.02-0.17	1.34-3.04	13-40
V	0.06-0.86	0.35-1.25	41-72
Cd	0-0.08	1.54-3.1	22-28
Ba	0-0.09	1.95-2.26	20-31
Cr	0.005-0.31	1.5-1.9	45-74
Sn	0-0.09	0.93-1.53	28-55
Mg	0.42-7.21	4.5-7.2	17-23

a/ The mass median diameter (MMD) represents the approximate "average" aerodynamic particle size, i.e., 50% of the particles are above this size and 50% are below.

Table 7. TRACE ELEMENT STACK EMISSIONS FROM COAL-FIRED POWER PLANTS (%)[a/]

Element	Valmont[b/]	Chalk Point[c/]	Widows Creek[d/]		Allen[e/]	
	A	A	A	B	A	B
Sb	14	32	88	-	0	27
As	14	33	-	-	8	3.4
Ba	-	6	40	26	0	0.31
Be	-	-	44	26	-	-
Bi	-	-	-	-	-	-
B	-	-	-	-	-	-
Br	-	98	-	-	-	100
Cd	-	-	82	-	0	2.3
Cl	-	-	95	-	-	97
Cr	-	10	35	39	0	1.2
Co	-	11	58	11	0	0.64
Cu	19	-	43	30	-	-
F	-	-	97	-	-	-
Fe	4.6	-	0	20	0	0.70
Pb	28	34	66	43	13	2.5
Mn	-	0	19	25	0	0.81
Hg	89	84	60	-	-	56
Mo	27	-	-	-	-	-
Ni	-	17	40	35	-	-
Se	80	52	12	-	45	12
Te	-	-	87	4.6	-	-
Tl	-	-	-	-	-	-
Sn	-	-	84	4.7	-	-
Ti	-	17	26	32	2	0.71
U	-	-	-	-	0	0.67
V	-	25	44	29	0	1.4
Zn	24	23	69	30	22	2.3
Zr	3.3	17	-	-	-	-

a/ Adapted from Reference 42.

b/ These data were obtained from a 180 Mw pulverized coal-fired unit. The unit was fitted with an economizer, a mechanical dust collector, and both an electrostatic precipitator and a wet scrubber which had been installed in parallel.

c/ These data were obtained from a 355 Mw wet bottom pulverized coal-fired unit. The unit was fitted with an economizer and an electrostatic precipitator. The study was not designed particularly to produce a mass balance.

d/ These data were obtained from a 125 Mw dry bottom pulverized coal-fired unit fitted with an economizer and a mechanical dust collector. The unit was not fitted with an electrostatic precipitator.

e/ These data were obtained in a 290 Mw crushed coal-fired cyclone unit fitted with an economizer and a high efficiency electrostatic precipitator.

f/ These estimates of trace element emissions apply strictly to pulverized coal-fired units only. They were made after examining the mass balances from the Valmont, Chalk Point, and Widows Creek units, all of which burn pulverized coal, and other trace element studies not involving mass balances.

Table 8. UPPER VALUE OF EXPECTED CONCENTRATIONS IN POWER PLANT FLUE GASES (UNCONTROLLED) COMPARED WITH MEASURED AMBIENT AIR CONCENTRATIONS[a]

Element	Upper value of expected concentration in flue gases for coal ($\mu g/Nm^3$)	Measured air concentrations ($\mu g/m^3$)
Aluminum	2,000,000	0.2-2.2
Antimony	1,000	Avg. 0.001 max. 0.160
Arsenic	5,000	Avg. 0.02
Barium	10,000	0.002-1.5
Beryllium	1,000	Avg. 0.0005 max. 0.008
Boron	10,000	No data
Bromine	5,000	0.0056-1.0
Cadmium	1,000	0.002-0.37, 0.001-0.05
Calcium[b]	1,000,000	0.02-0.39
Chlorine	500,000	0.07-2.9
Chromium	5,000	Avg. 0.015 max. 0.33
Cobalt	2,000	Avg. < 0.0005 max. 0.060
Copper	10,000	Avg. 0.09 max. 10.0
Fluorine	10,000	No data
Iron	2,500,000	Avg. 1.58 max. 22.0
Lead	10,000	Avg. 0.79 max. 8.50
Manganese	10,000	Avg. 0.10 max. 9.98
Mercury	100	0.0001-0.210
Molybdenum	5,000	Avg. < 0.005-0.78
Nickel	5,000	Avg. 0.032 max. 0.690
Selenium	500	0.003-0.009
Silver	100	0.0002-0.004
Tellurium	100	No data
Thallium	1,000	No data
Tin	1,000	Avg. 0.02 max. 0.50
Titanium	100,000	Avg. 0.04 max. 1.10
Uranium	500	No data
Vanadium	5,000	0.1-1.0
Yttrium	1,000	No data
Zinc	10,000	Avg. 0.67 max. 58
Zirconium	10,000	0.0005-0.08

a/ Adapted from Reference 43.

b/ Calcium in fly ash is usually present in the combined form primarily as glassy aggregates which are relatively inert.

SUMMARY OF SIZE/COMPOSITION OF PARTICULATE EMISSIONS

Particle size distribution data for fly ash from coal-fired power plants show a mass median diameter of about 5 μm at the outlet of the control device compared to 17 μm at the inlet, illustrating the fact that emission controls have a higher collection efficiency for larger particles. On a number basis, this means that there are many more smaller particles being emitted to the atmosphere, thus resulting in an increased probability for atmospheric reactions.

Analysis of fly ash particulate compositions indicates that the major constituents are SiO_2, Al_2O_3, CaO, and Fe_2O_3 in the western coals and SiO_2, Al_2O_3, and Fe_2O_3 in the eastern coals. Trace elements such as Pb, Cd, V, Se, As, Ni Cr, etc., are also present in fly ash. Furthermore, these trace materials exhibit pronounced concentration increases with decreasing particle sizes.

ANALYSIS OF INTERACTIONS BETWEEN PARTICULATE AND SULFUR-CONTAINING GASES

Particulate-SO_x interactions are complex in nature and do not appear to be fully understood. Three major processes were selected by which particulates could interact with sulfur-containing gases to lower the pH of rainfall. Order-of-magnitude calculations for reaction rates for each process based on existing information for size distribution, chemical composition, physical properties and measured chemical reactivity of fly ash from coal-fired power plants were attempted. A fourth mechanism which can directly oxidize SO_2 in the presence of light was also considered. The four mechanisms and their definitions, as used here, are listed below.

1. Absorption-oxidation of SO_2 by particulate,
2. Direct catalytic oxidation of SO_2 by particulate,
3. Adsorption/chemical reaction of SO_2 by particulate, and
4. Photolytic oxidation of SO_2.

The term "absorption-oxidation" in this discussion refers to catalysis by particulates in the presence of <u>significant</u> amounts of water so that SO_2 solubility, liquid phase diffusion, and droplet size are the key parameters in determining the overall SO_2 conversion rate along with the catalytic activity of fly ash.

Direct catalytic oxidation of SO_2 by particulate refers to the oxidation of SO_2 catalyzed by fly ash and other suspended particulates in the presence of relatively small quantities of adsorbed water. At low relative humidities up to about 40%, fly ash and other suspended particulate would probably be covered with only a fraction of a monolayer of adsorbed water. Under these conditions, effects of SO_2 solubility, pH and bulk diffusion on the overall reaction rate would be quite different than in the first mechanism defined above.

Adsorption/chemical reaction of SO_2 by particulate is a removal process unlike the two mechanisms defined above which are acid generation processes. SO_2 removal by this mechanism can occur either as physical adsorption or as chemisorption.

Photolytic oxidation of SO_2 may be defined as SO_2 conversion in the presence of sunlight. This is an acid generation mechanism.

A review of existing rate data disclosed that there were so many different forms of reported rate data and different reaction configurations that an order-of-magnitude comparison of any two given experiments was usually not possible without significant data reduction. The following discussion includes the method of analysis which was used in analyzing published rate data, and an individual discussion of each mechanism.

METHOD OF ANALYSIS OF PUBLISHED RATE DATA

A simple procedure of recalculating the published data in terms of "differential" or instantaneous forward reaction rates was adopted. The data were normalized to unit mass of the catalytic solid, as is the usual practice in heterogeneous rate studies.[44] It was possible using this procedure to then directly compare experimental results obtained from both steady-state flow and batch reaction experiments.

The differential reaction rate was calculated from reported experimental data according to the method given by Levenspiel.[45] Two different equations were used, depending on whether a batch (static) or flow reactor system were used. The molar rates calculated in this manner are directly comparable regardless of which type of experimental reactor was used. For a flow reactor, the differential rate is calculated from the following equation:

$$r_{SO_2} = \frac{F_{SO_2}\,\Delta X}{\Delta V} \qquad (1)$$

where r_{SO_2} = differential rate of conversion of SO_2, mmoles/m^3-min*

F_{SO_2} = molar feed rate of SO_2, mmoles/min

$\Delta X = X_f - X_i$

where X_f and X_i are fractions of SO_2 converted at points f and i of the reactor.

ΔV = volume increment (m^3)

For a static or batch reactor experiment, the reaction time is equivalent to reactor length in a fixed-bed flow reactor. The differential molar rate is calculated from the following equation.[45]

$$r_{SO_2} = \frac{N_{SO_2} \Delta X}{V \Delta t} \qquad (2)$$

where N_{SO_2} = initial number of mmoles of SO_2, $\Delta t = t_f - t_i$, and ΔX and V have the same representation as that presented above.

A number of field studies have been made in which concentrations of SO_2, SO_3, and sulfates were measured in the power plant plume. Much of these data have been summarized in recent EPA studies as part of project Midwest Interstate Sulfur Transport and Transformation (MISTT).[46] There is wide variation in the rates of SO_2 sulfation observed in these studies (from about 0 to 50%/hr) and it is difficult to relate the oxidation rate to fundamental rate parameters: temperature, relative humidity, and sunlight intensity.[46] The complexities involved in attempting to determine SO_2 oxidation rates from field data have been discussed by Hales et al.[47]

Due to the above reasons, the analysis of SO_2 oxidation catalyzed by particulates was limited, as far as possible, to studies performed under controlled, laboratory conditions.

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* mmoles denotes millimoles.

ABSORPTION-OXIDATION OF SO_2 BY PARTICULATE

This phenomenon refers to catalysis by particulate in the presence of large amounts of water and is frequently known as "precipitation scavenging,"[47] i.e., oxidation in the liquid phase in cloud droplets, or during periods of actual rainfall. However, kinetics derived from this assumed mechanism have also been used to predict sulfation rates in power plant plumes during periods of moderate relative humidity, as shown in the recent analytical study by Freiburg.[48]

There is direct evidence for the activity of fly ash from coal-fired plants in catalyzing the oxidation of SO_2 to SO_3 in the liquid phase.[49] The fly ash samples tested in the referenced study included: (a) a sample of aged NBS fly ash (from Potomac Electric Power Company), and (b) samples of fly ash collected from the pulverized coal-fired Salem Harbor Station. Catalytic activities for SO_2 oxidation in aqueous solution were found to be comparable for the various fly ash samples tested, regardless of aging. The initial activity of fly ash was approximately 11.1% of the activity of ferrous chloride as originally determined by Junge and Ryan[50] and later reconfirmed by GCA.[49] The results are depicted in Figure 23.

In Figure 23, the solution pH was measured in the bulk aqueous phase using conventional pH electrodes (i.e., by measurement of bulk solution conductivity). Total solution volume was approximately 30 cc. As indicated in the figure, the water-to-fly ash ratio was approximately 167 liters/g.

The mechanism by which gaseous SO_2 can be converted to sulfate in droplets was first reported by Junge and Ryan.[50] They described the oxidation of SO_2 in solution as nonphotolytic in nature and strongly inhibited by hydrogen ions. They measured SO_2 conversion rates in aqueous solutions of $MnCl_2$, $CuCl_2$, $FeCl_2$, $CoCl_2$, NaOH, NaCl, and distilled water. HCl or citric acid was used for pH adjustment. In a recent study[10] the activity of $FeCl_2$ was measured by an experimental technique similar to that of Junge and Ryan. The results of the earlier study were confirmed and the activity of several fly ash samples for oxidation of dissolved SO_2 was also determined. A summary of differential rate data recalculated from data reported by several investigators is presented in Table 9.

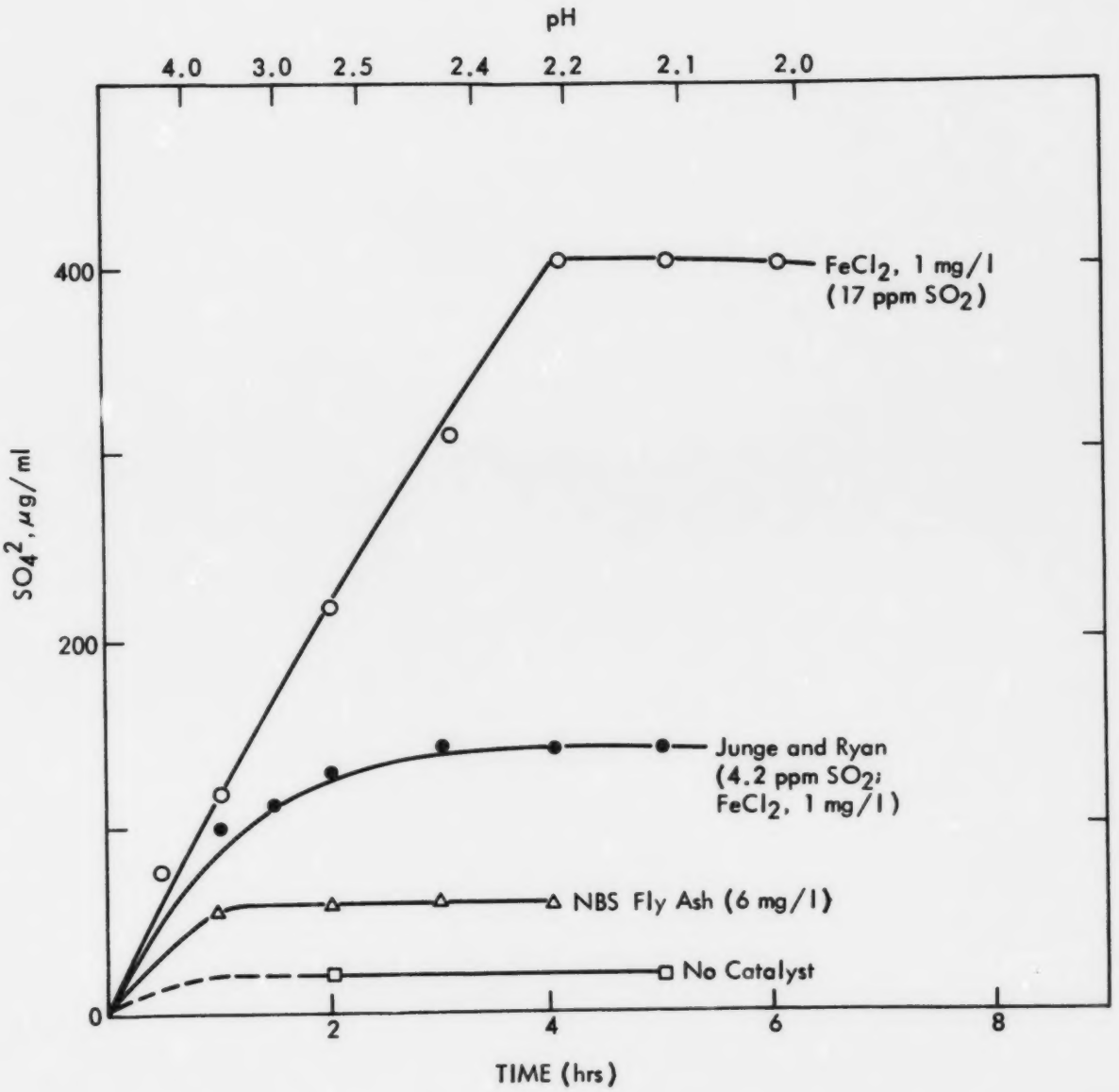

Figure 23. SO_2 aqueous oxidation rates[49/]

Table 9. SUMMARY OF PUBLISHED RATE DATA FOR OXIDATION OF DISSOLVED SO_2 (ABSORPTION/OXIDATION MECHANISM)

Metal ion (or metal salt)	Metal concentration (mmole/m^3)	$[H^+]$ (mmole/m^3)	$[SO_2]$ (ppm)[a]	Temperature (°C)	Differential conversion rate (mmole/m^3-min)	Differential conversion rate (mmole/m^3-min-g)	Reference
$MnSO_4$[b]	0.200	-	5.6-137	25	0.042	1.391	51
$MnSO_4$[b]	0.075	-	5.6-137	25	0.018	1.593	51
H_2O[c]	0.000	ND	1.0	[g]	8.12×10^{-3}	8.12×10^{-9}	52
H_2O[c]	0.000	ND	50	[g]	16.5×10^{-3}	16.5×10^{-9}	52
H_2O[c]	0.000	ND	4,300	[g]	13.5×10^{-3}	13.5×10^{-9}	52
$MnCl_2$	7.90	ND	[e]	[g]	19.02	19.02	50
$CuCl_2$	7.40	ND	[e]	[g]	11.51	11.51	50
$FeCl_2$	7.90	3.16×10^3	[e]	[g]	9.66	9.66	50
$CoCl_2$	7.70	ND	[e]	[g]	2.83	2.83	50
NH_4OH	29.38	ND	[e]	[g]	2.83	2.83	50
NaCl	17.11	ND	[e]	[g]	0.23	0.23	50
H_2O	0.000	ND	[e]	[g]	0.17	0.17	50
Fe^{3+}	1,420	4.074×10^4	[f]	10	103.5	1.305	53
Fe^{3+}	1,420	3.548×10^4	[f]	10	115	1.45	53
Fe^{3+}	1,420	3.090×10^4	[f]	10	157	1.98	53
Fe^{3+}	1,420	2.455×10^4	[f]	10	260	3.28	53
Fe^{3+}	1,420	1.950×10^4	[f]	10	411	5.18	53
Fe^{3+}	1,420	1.549×10^4	[f]	10	738	9.31	53
Fe^{3+}	1,420	1.259×10^4	[f]	10	1,167	14.72	53
Fe^{3+}	180	1.778×10^4	[f]	10	45	4.48	53
Fe^{3+}	180	1.000×10^4	[f]	10	36	3.58	53
Fe^{3+}	180	3.981×10^3	[f]	10	398	39.60	53
Fe^{3+}	180	2.239×10^3	[f]	10	844	83.96	53
Fe^{3+}	740	1.906×10^4	[f]	10	66	1.60	53
Fe^{3+}	740	1.000×10^4	[f]	10	163	3.94	53
Fe^{3+}	21,500	6.17×10^4	[f]	10	1,207	1.01	53
Fe^{3+}	10,600	6.17×10^4	[f]	10	479	0.84	53
Fe^{3+}	5,310	6.17×10^4	[f]	10	163	0.55	53
Fe^{3+}	4,800	6.17×10^4	[f]	10	130	0.48	53
Fe^{3+}	3,930	6.17×10^4	[f]	10	106	0.48	53
Fe^{3+}	2,650	6.17×10^4	[f]	10	72	0.49	53
Fe^{3+}	1,420	6.17×10^4	[f]	10	32	0.40	53
$FeCl_2$	7.90	[d]	[e]	[g]	20.2	20.20	49
NBS fly ash	-	[d]	[e]	[g]	9.25	1.54	49
In the absence of catalyst	0.000	[d]	[e]	[g]	1.78	1.78×10^{-6}	49

[a] Concentration in the gas phase, except as noted.
[b] Aerosol diameter (dry) = 0.51-0.81 μ; aerosol diameter (wet) = 1.8-3.7 μ; aerosol is stable at relative humidity, > 95%.
[c] Distilled water droplets (400-900 μ) at 94% relative humidity.
[d] pH decreased from 7 to about 2 during the reaction.
[e] A dilute mixture of SO_2 in air was bubbled into a 30-cc volume of distilled water and catalyst.
[f] Vapor-phase concentration of SO_2 was not determined; concentration in the liquid phase varied from 1.0-1.5 moles/m^3.
[g] Reaction temperature was not reported; however, it is obvious from the discussion that the experiment was performed under laboratory ambient conditions.
[h] Differential conversion rates estimated from concentrations of $SO_4^=$ measured after 3-hr reaction time.
ND = Not determined.

From Table 9, it is evident that oxidation rates for SO_2 in bulk aqueous solution are at least three orders-of-magnitude faster in the presence of most soluble salts and undissolved fly ash than in distilled water. Ammonium hydroxide also has a significant influence in accelerating the oxidation rate. The oxidation rate is highly dependent upon solution pH; however, there is insufficient information to permit a direct comparison between any two salts at this time. The overall range of values is probably representative of the expected range for the catalytic materials for which quantitative data could be found. Comparative rate data for SO_2 oxidation catalyzed by particulate in the absence of a bulk H_2O phase are presented next.

DIRECT CATALYTIC OXIDATION OF SO_2 BY PARTICULATE

This mechanism refers to SO_2 oxidation catalyzed by fly ash and other suspended particulates in the presence of small quantities of adsorbed water as opposed to absorption/oxidation discussed above which is in the presence of large amounts of water.

An order-of-magnitude calculation made using the BET theory[54] indicates that at 25°C, fly ash and other suspended particulates would be covered with less than a monolayer of water at relative humidities up to 60 to 70%. At 90% relative humidity, the predicted coverage is approximately five monolayers. One other source[55] estimates that at 27°C, monolayer coverage would occur at approximately 40% of saturation.

There were relatively few data on the rate of SO_2 oxidation under these conditions even though the data, when converted to differential conversion rates, were typically higher than for oxidation of dissolved SO_2 by one or two orders-of-magnitude on a unit weight basis. Comparative rate data for a number of cations commonly found in coal fly ash as either minor or trace elements are presented in Table 10.

Rate data included in Table 10 are based only on reported data in which particulates were heated to combustion temperature prior to testing. Rate measurements included were either made at steady state or corrected for the anomalously high initial activity which results when a large ratio of particulate to SO_2 is used in the measurements.

Measurements of SO_2 oxidation in the presence of various particulates have been reported by Urone et al.[58] They were not included here because (a) it was not possible to distinguish between initial and equilibrium rates, and (b) it was not possible to determine what fraction of the SO_2 concentration decrease resulted from SO_2 chemisorbed on the

Table 10. SUMMARY OF PERTINENT SO_2 OXIDATION RATE DATA FOR CATALYSIS BY METAL SALTS AND OXIDES

Catalyst	Total catalyst weight (g)[a]	Weight oxide/salt (mg)[b]	SO_2 concentration (influent) (ppm)	Effective reaction volume (cc)	Feed rate (mmole/min)	Conversion (%)	Differential conversion rate (mmole/min-m^3-g)[c]
$MnSO_4$[d]	15.5	0.51	3.3	23.9[i]	[h]	36.5	185.4[k]
$MnCl_2$[d]	6.375	0.255	3.3	23.9[i]	6.24×10^{-6}	5.2	53.2
$CuSO_4$[d]	[h]	0.15	14.4	78.2[i]	[h]	6.8	36.5[k]
NaCl[d]	[h]	0.36	14.4	78.2[i]	[h]	5.2	15.2[k]
SnO_2[e]	59.6	4,768	3,058	101.1[i]	0.312	19.2	124.3
BaO[e]	58.4	4,672	3,058	99.1[i]	0.307	19.2	127.4
Cr_2O_3[e]	62.8	5,024	3,058	106.5[i]	0.288	17.1	91.9
BaO + SnO[e]	59.2	4,736	3,058	100.4[i]	0.290	14.6	89.2
Cr_2O_3 + BaO[e]	56.0	4,480	3,058	95.0[i]	0.288	14.0	94.9
V_2O_5[e,f]	9.2	736	3,058	15.6[i]	0.277	2.1	506.0
V_2O_5[f,g]	8.8	704	4,329	14.9[i]	0.215	0.6	123.3

[a] Weight of catalyst and support.
[b] Weight of active metal salt/oxide.
[c] For definition, see Eq. (1) and (2).
Volume per unit time (molar feed volume times fractional conversion), mmole/min.
[d] Hydrous aerosols supported by Teflon beads. Reaction conditions--23° C, 740 mm Hg, relative humidity = 95%.[56]
[e] Metal oxides supported on Fuller's Earth; conditions--23.9° C, 1 atm, SO_2 = 2.28 torr (0.3% by volume), O_2 = 21.28 torr (2.8% by volume), N_2 = 377.89 torr (82.15% by volume), CO_2 = 111.72 torr (14.70% by volume), NO_x = 0.38 torr (0.05% by volume), and feed concentration = 0.125 gmoles/m^3.[57]
[f] Vanadium oxide promoted with 20% SeO_2.
[g] Reaction conditions are the same as described in Note e, except 148.9° C.
[h] Data either not determined or not reported.
[i] Calculated as the product of the mean residence time times the gas flow rate.
[j] Assuming a packed density of 36.816 lb/ft^3.
[k] Estimated from reported first-order rate constants.

surface of the particulate investigated. For example, high conversion rates were reported in the presence of alumina and calcium aluminum oxide particulates. In the case of alumina, the initial reaction involves reaction of SO_2 with the particulate itself, rather than formation of gaseous SO_3. Initial products are solid sulfates, sulfites, and sulfides which remain bonded to the solid surface up to very high temperatures.[59] These factors have apparently not been considered in Reference 58.

Although not usable for quantitative purposes, the study of Urone et al.[58] yields some extremely useful qualitative results. Significant oxidation rates were measured for Fe_2O_3, Cr_2O_3, PbO, PbO_2, and V_2O_5.[58] It was also found that at an intensity of ultraviolet light approximately seven times greater than expected under ambient conditions, there was relatively little enhancement of reaction rates over any of the particulates tested. In contrast to photolytic oxidation, Urone et al., reported relatively little effect of NO_2, hydrocarbons, and relative humidity on the oxidation rates catalyzed by particulates.[58]

ADSORPTION BY PARTICULATE (ACID REMOVAL PROCESSES)

Relatively little data are available which are directly applicable to acid removal processes. The laboratory studies by Bienstock, Field, and Meyers are pertinent in that they attempted to study the rate and mechanism of SO_2 adsorption from simulated flue gases.[60,61] Their simulated flue gas was a mixture of gases--0.3% sulfur dioxide, 13% carbon dioxide, 6% oxygen, 6.7% water vapor, and 74% nitrogen. This gas mixture was pumped through fixed beds of oxides of magnesium, cobalt, and copper; alkalized alumina; and activated charcoal. They found that sulfur dioxide was more efficiently removed from the mixture at 330°C than at 130°C. Adsorption increased with temperature and water vapor.[60-61]

The preceding brief discussion indicates that particulates may function as adsorbents in removing SO_2 from the atmosphere. Regardless of whether the SO_2, SO_3, sulfites, and sulfates are irreversibly removed from the atmosphere in the form of insoluble, chemisorbed species, the maximum removal capacity of fly ash is determined by the monolayer adsorption capacity. Order-of-magnitude calculations to determine the monolayer adsorption capacity and fractional removal capacity of fly ash as a function of particle size, geometric surface area, and probable discharge rates of fly ash and SO_2 are presented next. The discussion assumes that none of the fly ash can serve to neutralize acidic species by dissolving in rainwater.

The maximum acid removal capacity of fly ash by chemisorption is based on monolayer adsorption capacity which is directly proportional to the specific surface area, in area per unit weight.[54] The predicted variation in surface area and adsorption capacity with particle size is depicted in Table 11. The particle size distribution is for a tangentially fired, pulverized coal-fired boiler.[62] In Table 11, specific fly ash surface area is calculated using an assumed particle density of 2.3 g/cc and the geometric surface area, calculated according to the following widely used equation.[55]

$$S = 6/\rho d$$

where S = specific surface area, m^2/g

ρ = particle density, g/cm^3

d = particle diameter, μm

The specific surface area calculated using Eq. (3) has been compared with experimentally determined surface area data for submicron aerosols obtained using both BET and electron microscope methods and is found to yield excellent agreement.[63]

The chemisorption capacity is calculated by assuming monolayer adsorption capacity and hexagonal close packing of SO_3 (as H_2SO_4) in the adsorbed surface layer. The total monolayer capacity of the selected fly ash is approximately 4.4 micromoles of H_2SO_4 (or SO_3) per gram of fly ash. By comparison, complete combustion of a 4% sulfur coal containing 10% ash by suspension-firing generates approximately 14.7×10^3 micromoles of H_2SO_4 (or SO_3) per gram of fly ash. Typical data for coal-fired plants (i.e., less than 4% sulfur) would indicate that the average coal-fired plant generates about 0.58 g of sulfur compounds per gram of fly ash with a mass ratio of SO_2:SO_3 of 53.0 (30 ppm SO_3).[55] On this basis, the ratio of total sulfur compounds in the flue gas would be 9,168 micromoles/g, and the ratio of SO_3 to fly ash would be 136.35 micromoles/g. This latter value exceeds the predicted monolayer capacity of 4.4 micromoles/g by more than one order-of-magnitude.

On the basis of this information, it is considered unlikely that fly ash from coal-fired combustion sources can play a significant role in removing acid sulfates from the atmosphere via chemisorption.

Table 11. SURFACE AREA AND MONOLAYER ADSORPTION CAPACITY OF FLY ASH FOR SO_3 AS A FUNCTION OF PARTICLE SIZE FOR A TYPICAL SIZE DISTRIBUTION

Median particle size (μm)	Weight fraction[a]	Specific particle surface[b,c] (m^2/g)	Total surface (m^2/g)	Adsorption capacity for SO_3 (as H_2SO_4) (g mole/g)
34.64	0.6333	0.075	0.0475	0.376×10^{-6}
9.80	0.1000	0.266	0.0266	0.211×10^{-6}
6.00	0.0718	0.435	0.0312	0.247×10^{-6}
3.45	0.0622	0.756	0.0470	0.372×10^{-6}
1.61	0.0956	1.620	0.1548	1.227×10^{-6}
0.83	0.0144	3.143	0.0453	0.358×10^{-6}
0.43	0.0064	6.067	0.0388	0.308×10^{-6}
0.16	0.0102	16.304	0.1663	1.317×10^{-6}
	0.9999		0.5575	4.416×10^{-6}

a/ Source: Ref. 62.

b/ $S = 6/\rho d$; S = surface area, m^2/g; ρ = particle density, g/cc; d = particle diameter, μm (Reference: Hillenbrand, L. J., "Chemical Composition of Particulate Air Pollutants, EPA-R2-73-216, March 1973).

c/ Assumed particle density for coal fly ash was 2.3 g/cc.

PHOTOLYTIC OXIDATION OF SO_2

In order to place the measured rates of SO_2 conversion by particulates into perspective, a comparison was made with reported photolytic reaction rate data contained in the literature. Table 12 summarizes reported rates of photolytic oxidation of SO_2 including the rate calculated in this study.

The maximum expected conversion rate was calculated using reported solar intensity and quantum yield data with assumed values for mixing height and light fraction absorbed. Urone et al.[70] report a maximum intensity of 7.70×10^{14} photons/cm^2-sec for the 3100 to 4000 Å region, and Sethi[71] reports a quantum yield of 2.63×10^{-3} molecules/photon. If 50% of the incident light is absorbed and the mixing height is 1,000 m, then the conversion rate is 1.01×10^{-6} mmole/min-m^3. Conversion rates reported in Table 12 are for strict photolytic reactions and can vary if the reactions take place in the presence of hydrocarbons and other photochemical oxidants.[69]

COMPARISON OF PARTICULATE-SO_x INTERACTIONS

Catalytic data summarized in Tables 9 and 10 can be used to predict SO_2 oxidation rates in the presence of fly ash particulates provided the composition ranges of the catalytically active elements are known. As the rate data in Tables 9 and 10 indicate, there are a large number of elements which may be active as catalysts in the form of oxides, chlorides, or sulfates and their catalytic activities can vary by over an order of magnitude. Also, for conditions shown in Tables 9 and 10, the gas phase oxidation rate is higher than the oxidation rate for dissolved SO_2. This result is pertinent to the analysis of sulfation occurring at or near ground level where ambient temperatures are higher and relative humidities lower than that observed in clouds.

Using rate data contained in Table 10 for different catalysts, the maximum expected SO_2 oxidation rates in a typical power plant stack have been calculated. These values are shown in Table 13. A stack temperature of 149°C (300°F) and a residence time of 5.9 sec (250,000 cfm, 14-ft stack diameter and 160-ft stack height) were assumed in the calculation. The expected maximum concentrations for the catalysts indicated in Table 13 were selected, at random, to include 90% of the reported data.[72] Coal composition data were compiled from approximately 20 literature reports.

Table 12. COMPARISON OF SOME SO_2 PHOTOCHEMICAL REACTION RATE STUDIES

$[SO_2]$ (ppm)	Relative humidity (%)	Rate of SO_2 conversion (%/min)[a]	Differential conversion rate (mmole/min-m^3)	Reference
5-30	32-91	$(1.7\text{-}3.3) \times 10^{-3}$	$(3.47\text{-}40.5) \times 10^{-6}$	64
0.2-0.6	50	0.11	$(9.0\text{-}26.9) \times 10^{-6}$	65
10-20	50	1.4×10^{-3}	$(5.72\text{-}11.4) \times 10^{-6}$	66
[b]	0	8.0×10^{-4}	$(24{,}000\text{-}98{,}000) \times 10^{-6}$	67
1,000	0	3.9×10^{-4}	159.4×10^{-6}	68
1,000	50	4.6×10^{-4}	188.0×10^{-6}	68
10-50	[c]	[c]	1.01 x 10-6	This study

[a] Recalculated based on reported data by adjusting experimental conditions to the maximum expected UV light intensities under ambient conditions. (Data taken from Ref. 69.)

[b] Sulfur dioxide concentrations were reported in terms of partial pressures--56-230 mm Hg.

[c] Not determined.

Table 13. ESTIMATED MAXIMUM RATES OF SO_2 OXIDATION IN FLUE GAS CATALYZED BY COMPONENTS PRESENT IN FLY ASH

Catalyst	Range of concentrations in coal (ppm)[72]	Expected maximum concentration in flue gas ($\mu g/Nm^3$)[a]	Differential reaction rate (mmole/g-sec-m^3)	Calculated maximum SO_2 conversion in stack (%)[c]
SnO_2	0-404	1,000	30.29[b]	1.3
BaO	0-3,000	10,000	31.04[b]	13.5
Cr_2O_3	0.89-1,690	5,000	22.39[b]	4.9
V_2O_5	0.38-500	5,000	123.3[b]	26.8
$MnSO_4$	1-2,000	10,000	45.2[b]	19.6
$CuSO_4$	0.02-800	10,000	8.9[b]	3.9

a/ Based on 10.0 Nm^3/kg (coal; assuming 100% of coal ash is converted to fly ash; upper values for metal concentrations in coal include approximately 90% of reported data.

b/ Conversion rate data from Table 10 adjusted for flue gas temperature of 149°C (300°F) and for time in seconds.

c/ Basis: 4% sulfur in coal; 10.0 Nm^3 flue gas per kilogram coal; stack gas temperature 149°C (300°F); stack residence time, 5.9 sec.

It is evident from Table 13 that there are a number of components in fly ash which are sufficiently active to convert up to 27% of the SO_2 to sulfate (or SO_3) in the stack at or near their maximum concentrations. It is unlikely that the maximum concentration of more than one active metal would occur in the same coal sample so that the highest conversion level of 26.8% (for vanadium pentoxide) will probably never be exceeded under actual conditons. One report claims that the average SO_2 conversion in flue gas from coal-fired plants is only about 1.5%.[55]

Table 14 presents an order-of-magnitude comparison between catalytic (i.e., gas phase) and photolytic reaction rates shown in Tables 10 and 12, respectively. Catalytic rates listed correspond to maximum reported particulate concentrations. Zero-order kinetics were assumed for the rate dependence on SO_2 partial pressure, i.e., no dilution effect was considered. The catalytic rate calculation further assumes (a) first-order rate dependence on O_2, and (b) negligible inhibition by sulfate products. Metal oxide and/or sulfate concentrations used in Table 14 are based on reported ambient measurements summarized from National Air Sampling Network Data and other sources.[72]

At the maximum reported ambient concentrations, all of the catalytically active materials for which quantitative rate data could be found are predicted to exhibit conversion rates higher than for photolytic oxidation. The highest conversion rate was calculated for vanadium pentoxide (3.61×10^{-3} mmole/min-m^3) which is a common component of fly ash from both coal, and in higher concentrations, from oil-fired power plants. On the basis of these data, the SO_2 oxidation rate in the presence of reported ambient levels of V_2O_5 exceeds the reported photolytic oxidation rates (1.01×10^{-6} mmole/min-m^3) by more than three orders of magnitude.

Reported residence times,* as summarized by Freiburg[53] range from about 8 to 120 hr or more. Calculated SO_2 residence times, as shown in Table 14, are based on average reported ambient concentrations of catalytic compounds and range from 67.4 to 380.5 hr if the primary air standard of 80 $\mu g/nm^3$ is used as the initial SO_2 concentration. However, if the maximum reported ambient levels of catalytic compounds are used, the SO_2 residence time is of the order of a few minutes.

On the basis of data presented here, catalytic oxidation mechanisms of SO_2 by trace and minor components in fly ash in the presence of significant amounts of water and in the presence of small amounts of water are both plausible mechanisms by which rapid SO_2 oxidation could occur. These could take place at or near ground level and in the absence of sunlight. There is insufficient quantitative data for either catalytic

* Residence time for assumed zero order kinetics is defined as the ratio of concentration to rate constant.

Table 14. COMPARISON OF PHOTOLYTIC OXIDATION OF SO_2 WITH ESTIMATED MAXIMUM RATES OF CATALYTIC OXIDATION

Catalyst	Range of reported ambient concentrations in air ($\mu g/Nm^3$)	Differential reaction rate (mmole/g-min-m^3) [a]	Estimated maximum atmospheric rate (mmole/min-m^3) [b]	Calculated average SO_2 residence time (hr) [c]
SnO_2	0.02 (avg.)-0.50	124.3	4.43×10^{-4}	70.0
BaO	0.002-1.5	127.4	1.36×10^{-3}	-
Cr_2O_3	0.015 (avg.)-0.33	91.9	2.16×10^{-4}	127.0
V_2O_5	0.05-1.0	506.0	3.61×10^{-3}	-
$MnSO_4$	0.10 (avg.)-9.98	185.4	1.85×10^{-3}	67.4
$CuSO_4$	0.09 (avg.)-10.0	36.5	3.65×10^{-4}	380.5
Photochemical	-	-	1.01×10^{-6} [d]	1,250.0

[a] Data from Table 10 (23.8-25°C).

[b] Maximum rate calculated by using the maximum reported elemental concentrations in ambient air and assuming (a) first-order rate dependence on oxygen, (b) zero-order dependence on SO_2, and (c) no inhibition of reaction rate by SO_3.

[c] Calculated from average reported ambient metal concentrations by assuming an initial SO_2 concentration in ambient air of 80 $\mu g/Nm^3$ (1.25×10^{-6} gmole/Nm^3).

[d] Data from Table 12.

mechanism presented here to determine the relative importance of oxidation in solution (e.g., in cloud droplets or in raindrops) versus the oxidation rate on "dry" particulate ("direct oxidation mechanism"). However, data presented here indicates that both mechanisms need to be considered in predictions of SO_2 oxidation rates in stack plumes. Although a large number of minor and trace elements can be demonstrated to have significant catalytic activity for SO_2 oxidation, the list of such elements is far from complete. The activity of vanadium pentoxide for this reaction is tentatively concluded to be much higher than for other metals, and this may have significant implication in terms of fuel substitution strategies. Finally, additional study is required to determine the probable length of time fly ash of various size fractions remains suspended and the relative catalytic reactivity of these different size fractions.

EFFECT OF PARTICULATE EMISSION CONTROL DEVICES ON CONVERSION REACTIONS

Components of fly ash such as Na_2O, K_2O, and CaO are alkaline in nature and fly ash which is collected in precipitators is also usually alkaline with a pH in the range of 6.5 to 10.5.[73] It has been suggested that the use of emission control devices on coal-fired power plants causes the removal of these alkaline materials and thereby removes the "neutralizing" agents in acid-forming reactions in the atmosphere.

Likens and Bormann[30] suggested that the use of particulate emission control systems removes the alkaline substances, consequently permitting appreciable quantities of SO_2 to be converted to acid. Gordon et al. have studied the acidity of rainfall around the Chalk Point Power Plant and report that pH values from sampling stations ranged from 3.0 to 5.7 with modal values between 3.6 and 4.0.[74] Gordon et al. propose that the acid rain arises from the conversion of SO_2 and possibly NO_2 in the plume to H_2SO_4 and HNO_3. They also suggest that these acids are partially neutralized by species such as NH_3 and basic metal oxide particulates.

At the present time, it is difficult to determine the quantitative effect of the removal of the alkaline metal oxides on acid rain formation processes. First, atmospheric reactions are complex in nature and insufficiently defined to precisely determine whether and to what extent these alkaline materials would prevent acid-forming reactions or neutralize the acid after it is formed. Secondly, if these alkaline materials are indeed captured in the control device then it is logical to assume that they are larger in size than those emitted to the atmosphere. If this is the case, then with no controls the alkaline materials may not have a long enough atmospheric residence time to influence reactions

or alternatively, would settle out closer to the power plants due to their size. The net result would be a decrease in their capability to "neutralize" acid-forming reactions in the atmosphere which are usually catalyzed by fine particulates which have a concentration of active trace elements and which can be dispersed over long distances. Also, coals used in the northeast are, most likely, eastern coals which are less alkaline than western coals. Therefore, this factor must also be considered in evaluating the "neutralizing" capacity of fly ash. In any case, the collection of any alkaline material by the control device clearly removes an agent which can neutralize an acid. Whether this removal results in significant shifts in the atmospheric reactions leading to acid rain cannot be conclusively documented.

CONCLUSIONS AND RECOMMENDATIONS

This study has examined pollutant emission trends and acid rain trends in the northeastern United States. Characteristics of particulates from power plants and interactions of particulates and sulfur-bearing gases have also been investigated.

Review and analysis of the technical literature confirms that particulate and sulfur oxide emissions are concentrated in the northeastern section of the United States. Historical trend data, however, do not show significant increases in these pollutants, which may be a result of increased emphasis on control of pollutants in recent years. Acid rain trend data are extremely limited but do seem to support an increase in acidity in rainwater over much of New England and sections of New York.

Characterization of particulates from power plants indicates a mass median diameter of about 5 μm for particulates at the control device outlet. Also, mass collection efficiencies are less than about 85% for 1-μm particulates and fall off rapidly for fractions in the submicron region. Chemical characterization of particulate streams shows the existence of catalytically active materials such as oxides and sulfates of iron, vanadium, chromium, manganese, etc. Data also indicate that some of these materials tend to concentrate in smaller particles and thus escape capture by most commonly used control systems. All of this focuses attention on the need to enhance control efficiencies for particulates in the submicron region and may provide the reason as to why reduction in mass emissions alone is not adequate to combat the problem.

Particulate-SO_2 interactions have been reviewed via four oxidation mechanisms for acid aerosol generation. Results indicate that oxidation of SO_2 catalyzed by active metal oxides in particulates from power plants both in the presence of significant quantities of H_2O and in the absence of large quantities of H_2O may be the more important reactions. SO_2 removal by adsorption is ruled out in the analysis. Photolytic oxidation of SO_2 catalyzed by hydrocarbons and other oxidants is a distinct possibility and warrants further investigation.

Shifts to fossil fuels other than coal may also make contributions to the acid rain problem, especially the use of fuel oil containing vanadium. Vanadium pentoxide, a product from fossil fuel combustion, has significant catalytic activity for SO_2 oxidation. The emission of vanadium may work to counter the expected decrease in acid rain resulting from decreased SO_2 emissions achieved through fuel switching strategies.

Future studies in this area should include a systematic evaluation of the various parameters such as catalyst type, concentration, temperature, relative humidity, etc., which affect the kinetics of SO_2 oxidation in order to identify the main rate-controlling factors. Presently available experimental data do not consider these variables in a systematic manner and are not amenable to direct comparison. Acid rain formation from nitrates and chlorides should be separately investigated even though currently available information supports the hypothesis that only about 25% of the acidity in rain is due to nitrates and less than 10% due to chlorides. Refinement of techniques to predict whether sulfates, nitrates or chlorides are contributory to the acidity in a particular rain sample should also be undertaken. The incorporation of mathematical modeling to include transportation effects of pollutants to areas of geographic interest is also recommended. Finally, meteorological methods which monitor rainfall in different states and regions of the U.S. should include pH measurement of rainwater on a routine basis if it is not already being done. This would eliminate the data gap that presently exists for some sections of the U.S. and for most sections on a recent basis.

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16. ABSTRACT The report gives results of an extensive review and analysis of the literature aimed at: studying historical trends of particulate, SOx, and NOx emissions and of acid rain in the northeastern U.S.; studying size and composition of particulates from power plants; and analyzing interactions between particulates and sulfur-bearing gases from coal-fired power plants. Particulate mass emissions from industrial and combustion sources project a rising trend, nationwide, if no additional controls are assumed. (With application of best controls, the trend projection is reversed.) SO2 emissions have been increasing nationwide since 1950; without additional controls and with a 5% industry growth, this trend is expected to continue. (If new source performance standards and state implementation plans become effective in 1978, SO2 emissions are expected to decrease.) NOx mass emissions have increased consistently since 1920; those for 1970 were more than 3 times those for 1920. The limited data available for ambient NOx levels is further complicated by inherent limitations of measurement techniques used to obtain the data. Information on acid rain in northeastern U.S. is extremely scarce. Available data indicates that precipitation in this region has become increasingly acidic over the years. A better assessment of the trend can be made only when better rainwater pH information becomes available.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Rain Acidity Dust Sulfur Oxides Nitrogen Oxides Catalysis Electric Power Plants Coal Combustion	Air Pollution Control Stationary Sources Acid Rain Particulate	13B 04A 07D 10B 11G 21D 07B 21B

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